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OF THE

ROYAL SOCIETY

OF NEW SOUTH WALES

FOR

1949

(INCORPORATED 1881)

VOLUME LXXXIII

Parts I-IV

EDITED BY

W. B. SMITH-WHITE, M.A., B.Sc.

Honorary Editorial Secretary

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VOLUME LXXXIII

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Part III*

Royal Society of New South Wales

OFFICERS FOR 1948-1949

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NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

𝕴 bequeath the sum of £   to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within   calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.]

The volumes of the *Journal and Proceedings* may be obtained at the Society's Rooms, Science House, Gloucester Street, Sydney.

Volumes				
Volumes	XI to	LIII (that is to 1919)	at	12/6 each
,,	LIV ,,	LXVIII (1920 to 1934)	,,	25/- ,,
,,	LXX ,,	LXXXII (1936 to 1948)	,,	25/- ,,
,,	LXXXIII onwards		,,	30/- ,,

Volumes I to X (to 1876) and Volume LXIX (1935) are out of print.
Reprints of papers are available.

LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales

as at April 1, 1949

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.

1944		Adamson, Colin Lachlan, Chemist, 36 McLaren-street. North Sydney.
1938	P 2	‡Albert, Adrien, D.Sc., Ph.D. *Lond.*, B.Sc. *Syd.*, A.R.I.C. *Gt. B.*, Professor of Medical Chemistry, The Australian National University, 183 Euston-road, London N.W.1.
1935		‡Albert, Michael Francois, " Boomerang," Billyard-avenue, Elizabeth Bay.
1898		‡Alexander, Frank Lee, Surveyor, 5 Bennett-street. Neutral Bay.
1941		‡Alldis, Victor le Roy, I.S., Registered Surveyor, Box 57, Orange, N.S.W.
1948		Anderson, Geoffrey William, B.Sc., 37 Elizabeth-street, Allawah.
1948	P 1	Andrews, Paul Burke, Department of Geology, University of Sydney ; p.r. 5 Conway-avenue, Rose Bay.
1930		Aston, Ronald Leslie, B.Sc., B.E. *Syd.*, M.Sc., Ph.D. *Camb.*, A.M.I.E. *Aust.*, Lecturer in Civil Engineering and Surveying in the University of Sydney ; p.r. 24 Redmyre-road, Strathfield. (President, 1948.)
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1945		Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 2	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 2	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill ; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1946	P 1	Barclay, Gordon Alfred, Chemistry Department, Sydney Technical College, Harris Street, Ultimo, N.S.W. ; p.r. 78 Alt Street, Ashfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1947		Beckmann, Peter, A.S.T.C., Lecturer in Chemistry, Technical College, Wollongong.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, " Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. (*Oxon.*), 6 Beechcroft-road, Oxford, England.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale ; p.r. 26A Wolseley-road, Mosman.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., " Holmleigh," Cecil-avenue, Pennant Hills.
1948		Blanks, Fred Roy., B.Sc. (Hons.), Industrial Chemist, 12 Culworth-avenue, Killara.
1946		Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carrabella-street, Kirribilli.
1933	P 29	Bolliger, Adolph, Ph.D., F.A.C.I., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.)
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., " Hills and Dales," Mittagong. (President, 1935.)
1939	P 17	Bosworth, Richard Charles Leslie, M.Sc., D.Sc. *Adel.*, Ph.D. *Camb.*, F.A.C.I., F.Inst.P., c.o. C.S.R. Co. Ltd., Pyrmont ; p.r. 41 Spencer-road, Killara.
1948		Boyd, Eric Harold, B.A., B.Sc., Dip.Ed., F.P.S., The King's School, Parramatta.

Elected		
1948		Boyd, Joan, B.SC. Hons. *Lond.*, DIP.ED. *Lond.*, The King's School, **Parramatta.**
1938		Breckenridge, Marion, B.SC., Department of Geology, The University of Sydney ; p.r. 19 Handley-avenue, Thornleigh.
1946		Breyer, Bruno, M.D., Ph.D., M.A., F.A.C.I., Lecturer in Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Sydney.
1919	P 1	Briggs, George Henry, D.SC., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney ; p.r. 13 Findlay-avenue, Roseville.
1942		Brown, Desmond J., M.SC. (*Syd.*), Ph.D. (*Lond.*), D.I.C., Department of Medical Chemistry, Australian National University, 183 Euston-road, London, N.W.1.
1935	P 7	Browne, Ida Alison, D.SC., Senior Lecturer in Palæontology, University of Sydney.
1945		Brown, Norma Dorothy (Mrs.), B.SC., Biochemist, 2 Macauley-street, Leichhardt.
1941		Brown, Samuel Raymond, A.C.A. *Aust.*, 87 Ashley-street, Chatswood.
1913.	P 22	‡Browne, William Rowan, D.SC., Reader in Geology, University of Sydney. (President, 1932.)
1947		Buchanan, Gregory Stewart, B.SC. (Hons.), Lecturer in Physical Chemistry, Sydney Technical College ; p.r. 52 Mary-street, Beecroft.
1940		Buckley, Lindsay Arthur, B.SC., 29 Abingdon-road, Roseville.
1946		Bullen, Keith Edward, M.A., B.SC. *N.Z.*, M.A. *Melb.*, Ph.D., SC.D. *Camb.*, F.R.S., Professor of Applied Mathematics, University of Sydney, Sydney, N.S.W.
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.SC. *Syd.*, F.R.A.C.S., " Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.SC., Professor of Anatomy in the University of Sydney.
1938	P 2	‡Carey, Samuel Warren, D.Sc., Professor of Geology, University of Tasmania, Tasmania.
1948		Carroll, Dorothy, B.A., B.SC., Ph.D., D.I.C., Secretary, Linnean Society of New South Wales, Science House, 157 Gloucester-street, Sydney.
1903	P 5	‡Carslaw, Horatio Scott, SC.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge ; Burradoo, N.S.W.
1945		Carter, Harold Burnell, B.V.SC., Research Officer, C.S.I.R., McMaster Laboratory, University Grounds, Sydney.
1944		Cavill, George William Kenneth, M.SC., c/o Department of Organic Chemistry, The University, Liverpool, Great Britain.
1913	P 4	‡Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S. ; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
1940		Chambers, Maxwell Clark, B.SC., c/o Coty (England) Ltd., 35-41 Hutchinson-street, Moore Park ; p.r. 58 Spencer-road, Killara.
1913	P 21	‡Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
1935	P 2	Churchward, John Gordon, B.SC.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
1941		Cohen, Max Charles, B.SC., 80 " St. James," Stanley-street, Sydney.
1940		Cohen, Samuel Bernard, M.SC., A.A.C.I., 8 Roseville-avenue, Roseville.
1940	P 2	Cole, Edward Ritchie, B.SC., 7 Wolsten-avenue, Turramurra.
1940	P 1	Cole, Joyce Marie, B.SC., 7 Wolsten-avenue, Turramurra.
1948		Cole, Leslie Arthur, Company Executive, 21 Carlisle-street, Rose Bay.
1940		Collett, Gordon, B.SC., 20 Duchess-avenue, Fivedock.
1948		Cook, Cyril Lloyd, M.SC., 176 Ben Boyd-road, Neutral Bay.
1946		Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1945		Coombes, Arthur Roylance, A.S.T.C. (chem.), 14 Georges River-road, Croydon.
1913	P 5	‡Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College ; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1937	P 8	Cornforth, Rita Harriet, D.Phil. (*Oxon.*), M.SC. (*Syd.*), c/o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
1940		Cortis-Jones, Beverly, M.SC., 62 William-street, Roseville.
1919		Cotton, Frank Stanley, D.SC., Research Professor in Physiology in the University of Sydney.

Elected.		
1909	P 7	‡Cotton, Leo Arthur, M.A., D.Sc., 113 Queen's Parade East, Newport Beach. (President, 1929.)
1941	P 1	Craig, David Parker, Lecturer in Inorganic Chemistry, University of Sydney; p.r. 62 Springdale Rd., Killara.
1921	P 1	‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street., Rockdale.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1948		Cymerman, John, Ph.D., D.I.C., A.R.C.S., B.Sc., A.R.I.C., Lecturer in Organic Chemistry, University of Sydney.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		‡Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., " Mélamere," Welham-street, Beecroft.
1906		‡Dixson, Sir William, " Merridong," Gordon-road, Killara.
1913	P 3	‡Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1947		Downes, Alan Marchant, B.Sc. (Hons.), Grandview-avenue, Croydon, Victoria.
1948		Doyle, Shirley Kathleen, B.Sc., Microbiologist to H. Jones & Co.; p.r. 74 Duntroon-avenue, Roseville.
1943		Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
1937	P 13	Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney; p.r. 40 Manning-road, Double Bay. (President, 1947.)
1948		Dunlop, Bruce Thomas, B.Sc., Schoolteacher, 77 Stanhope-road, Killara.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. " Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 40	Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney, Sydney.
1945		Eade, Ronald Arthur, B.Sc., 21 Steward-street, Leichhardt.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
1940		Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
1937		English, James Roland, L.S., Sydney.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1944		Erhart, John Charles, Chemical Engineer, c/o "Ciba" Coy., Basle, Switzerland.
1908		‡Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. Lond., A.R.A.I.A., 6 Major-street, Coogee.
1944		Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 338 Chapple-street, Broken Hill.
1909	P 7	‡Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
1940		Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1933		Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street, Sydney.
1879		‡Foreman, Joseph, M.R.C.S. Eng., L.R.C.P. Edin., " The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., 35 Riversdale-road, Hawthorn, Victoria.
1905		‡Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1943		Frederick, Robert Desider Louis, B.E., 162 Buckley-street, Essendon, W.5, Victoria.
1940		Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
1944	P 2	Friend, James Alan, 16 Kelburn-road, Roseville.
1945		Furst, Hellmut Friedrich, B.D.S. (Syd.), D.M.D. (Hamburg), Dental Surgeon, 158 Bellevue-road, Bellevue Hill.
1948		Gardiner, Edward Carson, Electrical Engineer in Charge of Construction at the Captain Cook Graving Dock, for the Department of Works and Housing p.r. 39 Spencer-street, Rose Bay.

Elected.

1935	P 2	Garretty, Michael Duhan, D.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria.
1939	P 4	Gascoigne, Robert Mortimer, Chemistry Department, University of Liverpool, England.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney ; p.r. " Wirruna," Belmore-avenue, Wollstonecraft.
1942	P 3	Gibson, Neville Allan, M.Sc., A.R.I.C., Industrial Chemist, 217 Parramatta-road, Haberfield.
1947		Gill, Naida Sugden (Miss), B.Sc., 45 Neville-street, Marrickville.
1947		‡Gill, Stuart Frederic, School Teacher, 45 Neville-street, Marrickville.
1940		Gillis, Richard Galvin, Senior Lecturer, Organic Chemistry, Melbourne Technical College ; p.r. 4 Tennyson-avenue, Caulfield, S.E.7, Victoria.
1948		Glasson, Kenneth Roderick, B.Sc., Geologist, Lake George Mines Ltd., Captain's Flat, N.S.W.
1945		Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney.
1947		Goldsworthy, Neil Ernest, M.B., Ch.M. *Syd.*, Ph.D., D.T.M. & H. *Camb.*, D.T.M. & H. *Eng.*, D.P.H. *Camb.*, 65 Roseville-avenue, Roseville.
1936		Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill.
1948		Gray, Charles Alexander Menzies, B.Sc., B.E., 75 Woniora-road, Hurstville.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture ; p.r. 151 Wollongong-road, Arncliffe.
1946		Gutmann, Felix, Ph.D., F.Inst.P., M.I.R.E., Commonwealth Research Fellow, Faculty of Agriculture, University of Sydney, Sydney.
1948		Gyarfas, Eleonora Clara, M.Sc. *Budapest*, Research Assistant, University of Sydney ; p.r. 53 Simpson-street, Bondi.
1947		Hall, Lennard Robert, B.Sc., Geological Survey, Department of Mines, Bridge-street, Sydney.
1945		Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, 15A Wharf-road, Longueville.
1892		‡Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney ; p.r. 23 March-street, Bellevue Hill.
1940	P 14	Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney.
1905	P 6	‡Harker, George, D.Sc., F.A.C.I. ; p.r. 89 Homebush-road, Strathfield.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1948	P 1	Harris, Clive Molville, Laboratory Assistant, Museum of Technology and Applied Science ; p.r. 12 Livingstone-road, Lidcombe.
1946		Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord ; p.r. 34 Nicholson-street, Chatswood.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1945		Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd. ; p.r. 10 Cremorne-road, Cremorne.
1938	P 4	Hill, Dorothy, M.Sc. *Q'ld.*, Ph.D. *Cantab.*, Geological Research Fellow, University of Queensland, Brisbane.
1946		Hinder, Nora (Miss), B.Sc. *Syd.*, 22 Chester-street, Epping.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd. ; p.r. " Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (*Aust.*), " St. Cloud," Beaconsfield-road, Chatswood.
1948	P 3	Hogarth, Julius William, 8 Jeanneret-avenue, Hunter's Hill.
1916		Hoggan, Henry James, A.M.I.M.E. *Lond.*, A.M.I.E. *Aust.*, Consulting and Designing Engineer, 81 Frederick-street, Rockdale.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Technical College, Granville.
1935		Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1938	P 9	Hughes, Gordon Kingsley, B.Sc., Department of Chemistry, University of Sydney, Sydney.
1947		Humpoletz, Justin Ernst, B.Sc. *Syd.*, 21 Belgium-avenue, Roseville.
1923	P 3	‡Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney ; p.r. " Belbooree," 10 Wandella-avenue, Roseville.

Elected.		
1943		Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville.
1942	P 1	Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
1946		Johnson, Guy Frederick, 644 Botany-road, Alexandria.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1948	P 1	Jopling, Alan Victor, B.Sc., B.E., 28 Cliff-street, Manly.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1935		Kelly, Caroline Tennant (Mrs.), Dip.Anth., " Eight Bells," Cast e Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove.
1948		Kimble, Frank Oswald, Engineer, 16 Evelyn-avenue, Concord.
1943		Kimble, Jean Annie, B.Sc., Research Chemist, 383 Marrickville-road, Marrickville.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.
1948		Knight, Oscar Le Maistre, B.E. Syd., A.M.I.C.E., A.M.I.E.Aust., Engineer, 10 Mildura-street, Killara.
1948		Koch, Leo E., Ph.D., D.Sc. (Cologne), Department of Geology, The University of Sydney.
1939	P 1	Lambeth, Arthur James, B.Sc., " Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., Box 21, P.O., Concord.
1946		Lederer, Michael, 67 Edgecliff-road, Bondi Junction.
1947		Le Fevre, Raymond James Wood, D.Sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney.
1936	P 2	Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 56	‡Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.)
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1947		Lloyd, James Charles, B.Sc. Syd., N.S.W. Geological Survey, 41 Goulburn-street, Liverpool.
1940	P 1	Lockwood, William Hutton, B.Sc., F. & A. Inspectorate, 64 H.Q., C.C.G., Minden, Germany.
1906		‡Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1947		Lowenbein, Gladys Olive (Mrs.), B.Sc. Melb., F.R.I.C. Gt. B., A.A.C.I., Director of Research, Australian Leather Research Association; p.r. " Cahors," No. 75, 117 Macleay-street, Potts Point.
1943		‡Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park.
1945		Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1948		Lyons, Lawrence Ernest, B.A., M.Sc., Lecturer in Chemistry, The University of Sydney; p.r. 13 Albert-road, Strathfield.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 84 Marine-parade, Maroubra.
1939	P 4	Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1943		McCoy, William Kevin, Analytical Chemist, c/o Mr. A. J. McCoy, 39 Malvern-avenue, Merrylands.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1948		McInnes, Gordon Elliott, Department of Geology, The University of Sydney; p.r. 46 Laycock-street, Bexley.

Elected.			
1906	P	2	‡McIntosh, Arthur Marshall, " Moy Lodge," Hill-street, Roseville.
1891	P	1	‡McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P	7	McKenzie, Hugh Albert, B.Sc., c/o Frick Chemical Laboratory, Princeton University, Princeton, New Jersey, U.S.A.
1943			McKern, Howard Hamlot Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo ; p.r. Flat 2, 42A, Waimea-street, Burwood.
1947			McMahon, Patrick Reginald, M.Agr.Sc. N.Z., Ph.D. Leeds, A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney.
1927			McMaster, Sir Frederick Duncan, Kt., " Dalkeith," Cassilis, N.S.W.
1943			McNamara, Barbara Joyce (Mrs.), M.B., B.S., Yeoval, 7.W.
1946			McPherson, John Charters, 14 Sarnar-road, Greenwich.
1946	P	1	McRoberts, Helen May, B.Sc., New England University College, Armidale.
1947			Magee, Charles Joseph, D.Sc.Agr. Syd., M.Sc. Wis., Chief Biologist, Department of Agriculture ; p.r. 4 Alexander-parade, Roseville.
1947			Maley, Leo Edmund, M.Sc., B.Sc. (Hons.), A.A.C.I., A.M.A.I.M.M., 116 Maitland road, Mayfield.
1940			Malone, Edward E., 33 Windsor-road, St. Mary's.
1947	P	8	Mapstone, George E., M.Sc., A.A.C.I., M.Inst.Pet., Chief Chemist of National Oil Pty. Ltd., Glen Davis ; p.r. 2 Anderson Square, Glen Davis, N.S.W.
1944			Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1946			May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill.
1935	P	1	Maze, Wilson Harold, M.Sc., Deputy Registrar, University of Sydney, Sydney.
1912			‡Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown ; p.r. 98 Sydney-road, Manly.
1929	P	25	Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, University of Sydney ; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.)
1941			Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1928			Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, " Walla Walla," Hull-road, Beecroft.
1940			Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd. 15 Shaw-avenue, Earlwood.
1941			Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P	28	Morrison, Frank Richard, A.A.C.I., F.C.S., Deputy Director, Museum of Technology and Applied Science, Harris-street, Ultimo.
1934			Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
1948			Mosher, Kenneth George, B.Sc., Geologist, Geological Survey, Department of Mines, Bridge-street, Sydney.
1944			Moye, Daniel George, B.Sc., Geologist, Warragamba Dam.
1946			Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney.
1948			Mulley, Joan W., Technical Officer, C.S.I.R. ; p.r. 4 Billyard-avenue, Elizabeth Bay.
1915			Murphy, Robert Kenneth, Dr.Ing., Chem., A.S.T.C., M.I.Chem.E., F.A.C.I., Principal, Sydney Technical College, Sydney.
1923	P	2	Murray, Colonel Jack Keith, B.A., B.Sc.Agr., Administrator, Territory of Papua-New Guinea, Government House, Port Moresby.
1948			Naylor, Betty Yvonne, B.Sc., 6 Niblick-avenue, Roseville.
1930	P	6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld.
1943			Neuhaus, John William George, 190 Old Prospect-road, Wentworthville.
1932			Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Professor of Botany, The University of Ceylon, Colombo, Ceylon.
1943			Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co. ; p.r. No. 2 Flat, corner Hendy-avenue and Rainbow-streets, Coogee.
1935			Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1945	P	1	Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T.
1938	P	1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., c/o C.S.I.R., 314 Albert-street, East Melbourne, Vic.
1920	P	4	‡Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney ; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)

Elected.		
1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
1940		Robertson, Rutherford Ness, B.SC. *Syd.*, PH.D. *Cantab.*, Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush ; p.r. Flat 4, 43 Johnston-street, Annandale.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1948		Rosenthal-Schneider, Ilse, PH.D., 48 Cambridge-avenue, Vaucluse.
1940		Ross, Jean Elizabeth, B.SC., Dip.Ed., 5 Stanton-road, Haberfield.
1948		Ross, Leonard Paul, B.SC., 137 Burwood-road, Enfield.
1945		Rountree, Phyllis Margaret, M.SC. *Melb.*, Dip.Bact. *Lond.*, Royal Prince Alfred Hospital, Sydney.
1945		Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory ; p.r. 83 Woniora-road, Hurstville.
1945		Sampson, Aileen (Mrs.), SC.Dip. (A.S.T.C., 1944), 9 Knox-avenue, Epping.
1941	P 3	Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.SC. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern ; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1948	P 1	Schafer, Harry Neil Scott, B.SC., 18 Bartlett-street, Summer Hill.
1946	P 1	Scott, Beryl (Miss), B.SC., Geology Department, University of Tasmania.
1940		Scott, Reginald Henry, B.SC., 3 Walbundry-avenue, East Kew, Victoria.
1933		Selby, Esmond Jacob, Dip.com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
1948		Sharp, Kenneth Raeburn, Geology Department, The University of Sydney ; p.r. Kitchener-road, St. Ives.
1938		Sheahan, Thomas Henry Kennedy, B.SC., Chemist, c/o Shell Co. of Aust., North Terrace, Adelaide.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.SC. *Melb.*, 43 Robertson-road, Centennial Park.
1948		Sherwood, Ian Russell, D.SC., F.A.C.I., Research Bacteriologist, Research Laboratory, Colonial Sugar Refining Co. Ltd., John-street, Pyrmont.
1945		Shulman, Albert, B.SC., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
1945	P 2	Simmons, Lewis Michael, B.SC. (Hons.) *Lond.*, PH.D. *Lond.*, F.A.C.I., Head of Science Department, Scots College ; p.r. The Scots College, Victoria-road, Bellevue Hill.
1948		Simonett, David Stanley, B.SC., Geography Department, The University of Sydney ; p.r. 14 Selwyn-street, Artarmon.
1943		Simpson, John Kenneth Moore, Industrial Chemist, " Browie," Old Castle Hill-road, Castle Hill.
1933		Slade, George Hermon, B.SC., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush ; p.r. " Raiatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, New College, Oxford, England.
1947		Smith-White, William Broderick, M.A. *Cantab.*, B.SC. *Syd.*, Department of Mathematics, University of Sydney ; p.r. 7 Henson-street, Summer Hill.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.SC., B.SC.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, " Araboonoo," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		‡Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney ; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1948	P 1	Stevens, Neville Cecil, B.SC., Geology Department, The University of Sydney ; p.r. 12 Salisbury-street, Hurstville.
1900	P 1	‡Stewart, J. Douglas, B.V.SC., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney ; p.r. " Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.SC., PH.D., Department of Biochemistry, The University, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney ; p.r. 79 Ocean-street, Woollahra.
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes ; Box 23, P.O., Burwood ; p.r. " Stonycroft," 10 Redmyre-road, Strathfield.

Elected.		
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney ; p.r. " Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. *Adel.*, c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.
1948		Swinbourne, Ellice Simmons, Organic Chemist, 183 Sydney-road, Balgowlah.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney ; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Squadron Leader, R.A.A.F., M.Sc., A.Inst.P., 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic.
1946		Thomas, Ifor Morris, M.Sc., Department of Zoology, University of Adelaide, Adelaide, S.A.
1919		Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney ; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
1923		Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, " Werrington," Manion-avenue, Rose Bay.
1943		Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney ; p.r. 120 Awaba-street, Mosman.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney ; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 10	‡Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney ; p.r. " Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.)
1948		Walker, Donald Francis, Surveyor, 13 Beauchamp-avenue, Chatswood.
1943		Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping.
1919	P 2	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney ; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1913	P 5	‡Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1944		Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T.
1921		‡Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett, Illoura-avenue, Wahroonga.
1919	P 1	Waterhouse, Lionel Lawry, B.E. *Syd.*, Reader in Geology in the University of Sydney.
1919	P 7	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor of Agriculture, University of Sydney ; p.r. " Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1944		Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney.
1911	P 1	‡Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney ; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1947		Webb, Gordon Keyes, A.F.I.A., A.C.I.S., Accountant, c/o Max Wurcker (1930) Pty. Ltd., 99 York-street, Sydney.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1947		Werner, Ronald Louis, Industrial Chemist, 25 Dine-street, Randwick.
1946		Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1943		Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood.

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HONORARY MEMBERS.

Limited to Twenty.

OBITUARY, 1948-49.

1909   Ernest Clayton Andrews.

1923   George Frederick Birks.

1932   Ernest Norman McKie.

1920   Edward Montague Wellish.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke " as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories ; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
"The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
"Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
"The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.
1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.
1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.
1947. "The Teachers of Geology in Australian Universities." By Professor H. S. Summers, D.Sc.
1948. "The Sedimentary Succession of the Bibliando Dome : Record of a Prolonger Proterozoic Ice Age." By Sir Douglas Mawson, O.B.E., F.R.S., D.Sc., B.E.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
1879 *George Bentham, C.M.G., F.R.S.
1880 *Professor Thos. Huxley, F.R.S.
1881 *Professor F. M'Coy, F.R.S., F.G.S.
1882 *Professor James Dwight Dana, LL.D.
1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

Awarded.
1885 *Sir Joseph Dalton Hooker, o.m., g.c.s.i., c.b., m.d., d.c.l., ll.d., f.r.s.
1886 *Professor L. G. De Koninck, m.d.
1887 *Sir James Hector, k.c.m.g., m.d., f.r.s.
1888 *Rev. Julian E. Tenison-Woods, f.g.s., f.l.s.
1889 *Robert Lewis John Ellery, f.r.s., f.r.a.s.
1890 *George Bennett, m.d., f.r.c.s. *Eng.*, f.l.s., f.z.s.
1891 *Captain Frederick Wollaston Hutton, f.r.s., f.g.s.
1892 *Sir William Turner Thiselton Dyer, k.c.m.g., c.i.e., m.a., ll.d., sc.d., f.r.s., f.l.s.
1893 *Professor Ralph Tate, f.l.s., f.g.s.
1895 *Robert Logan Jack, ll.d., f.g.s., f.r.g.s.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, c.m.g., f.r.g.s.
1900 *Sir John Murray, k.c.b., ll.d., sc.d., f.r.s.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, c.m.g., f.l.s.
1903 *Alfred William Howitt, d.sc., f.g.s.
1907 *Professor Walter Howchin, f.g.s., University of Adelaide.
1909 *Dr. Walter E. Roth, b.a.
1912 *W. H. Twelvetrees, f.g.s.
1914 Sir A. Smith Woodward, ll.d., f.r.s., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, m.a., d.sc., f.r.s.
1917 *Professor Sir Edgeworth David, k.b.e., c.m.g., d.s.o., m.a., sc.d., d.sc., f.r.s., f.g.s.
1918 *Leonard Rodway, c.m.g., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, f.g.s.
1921 *Joseph James Fletcher, m.a., b.sc.
1922 *Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, k.c.m.g., m.a., d.sc., f.r.s.
1924 *Joseph Henry Maiden, i.s.o., f.r.s., f.l.s., j.p.
1925 *Charles Hedley, f.l.s.
1927 Andrew Gibb Maitland, f.g.s., " Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, b.a., f.g.s., 32 Benelong Crescent, Bellevue Hill.
1929 Professor Ernest Willington Skeats, d.sc., a.r.c.s., f.g.s., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, b.a., b.e., d.sc., Government Geologist, Geological Survey Office, Adelaide.
1931 *Robin John Tillyard, m.a., d.sc., sc.d., f.r.s., f.l.s., f.e.s., Canberra, F.C.T.
1932 *Frederick Chapman, a.l.s., f.r.s.n.z., f.g.s., Melbourne.
1933 Walter George Woolnough, d.sc., f.g.s., Department of the Interior, Canberra, F.C.T.
1934 *Edward Sydney Simpson, d.sc., b.e., f.a.c.i., Carlingford, Mill Point, South Perth, W.A.
1935 *George William Card, a.r.s.m., 16 Ramsay-street, Collaroy, N.S.W.
1936 Sir Douglas Mawson, kt., o.b.e., f.r.s., d.sc., b.e., University of Adelaide.
1937 J. T. Jutson, b.sc., ll.b., 9 Ivanhoe-parade, Ivanhoe, Victoria.
1938 *Professor H. C. Richards, d.sc., The University of Queensland, Brisbane.
1939 *C. A. Sussmilch, f.g.s., f.s.t.c., 11 Appian Way, Burwood, N.S.W.
1941 Professor Frederic Wood Jones, m.b., b.s., d.sc., f.r.s., Anatomy Department, University of Manchester, England.
1942 William Rowan Browne, d.sc., Reader in Geology, The University of Sydney, N.S.W.
1943 Walter Lawry Waterhouse, m.c., d.sc.Agric., d.i.c., f.l.s., Reader in Agriculture, University of Sydney.
1944 Professor Wilfred Eade Agar, o.b.e., m.a., d.sc , f.r.s., University of Melbourne, Carlton, Victoria.
1945 Professor William Noel Benson. b.a., d.sc., f.g.s., f.r.g.s., f.r.s.n.z., f.g.s.Am., University of Otago, Dunedin, N.Z.
1946 Black, J. M., a.l.s. (*honoris causa*), Adelaide, S.A.
1947 *Hubert Lyman Clark, a.b. d.sc., ph.d., Hancock Foundation, u.s.c., Los Angeles, California.
1948 Walkom, Arthur Bache, d.sc., Director, Australian Museum, Sydney.

AWARDS OF THE JAMES COOK MEDAL.

Bronze Medal.

Awarded annually for outstanding contributions to science and human welfare in and for the Southern Hemisphere.

1947 Smuts, Field-Marshal The Rt. Hon. J. C., p.c., c.h., k.c., d.t.d., ll.d., f.r.s., Chancellor, University of Capetown, South Africa.
1948 Houssay, Bernado A., Professor of Physiology, Instituto de Biologia y Medicina Experimental, Buenos Aires, Argentina.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled " The Aborigines of New South Wales."

1882 Andrew Ross, M.D., Molong, for paper entitled " Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal.

1884 W. E. Abbott, Wingen, for paper entitled " Water supply in the Interior of New South Wales."

1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled " The Tin deposits of New South Wales."

1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled " Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled " The Anatomy and Life-history of Mollusca peculiar to Australia."

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled " List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled " The Australian Aborigines."

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled " The Microscopic Structure of Australian Rocks."

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled " The effect which settlement in Australia has produced upon Indigenous Vegetation."

1894 J. V. De Coque, Sydney, for paper entitled the " Timbers of New South Wales."

1894 R. H. Mathews, L.S., Parramatta, for paper entitled " The Aboriginal Rock Carvings and Paintings in New South Wales."

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled " The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."

1896 Rev. J. Milne Curran, Sydney, for paper entitled " The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

1948 Waterhouse, Walter L., M.S., D.Sc.Agr., D.I.C., F.L.S., Sydney, in recognition of his valuable contributions in the field of agricultural research.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £75.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past six years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.

1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.

1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.

1947 John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.

1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.

1940 G. J. Burrows, B.Sc., University of Sydney. `

1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.

1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.

1946 Briggs, L. H., D.Phil. (*Oxon.*), D.Sc. (*N.Z.*), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.

1948 Ian Lauder, M.Sc., Ph.D., University of Queensland, Brisbane.

Royal Society of New South Wales

REPORT OF THE COUNCIL FOR THE YEAR ENDING 31st MARCH, 1949.

PRESENTED AT THE ANNUAL GENERAL MEETING OF THE SOCIETY, 6TH APRIL, 1949
(RULE XXVI).

The membership of the Society at the end of the period under review stood at 354.   Thirty-eight new members were elected during the year, the Council having made a special effort towards increased enrolment ; however, twelve members were lost by resignation and four, who were in arrears with subscriptions, were removed from the register.   Four members have been lost to the Society by death since 1st April, 1948 :

>   Ernest Clayton Andrews (1909).
>
>   George Frederick Birks (1923).
>
>   Ernest Norman McKie (1932).
>
>   Edward Montague Wellish (1920).

Professor Marcus L. Oliphant, B.Sc., Ph.D., F.R.S., and Professor Sir Robert Robinson, M.A., D.Sc., F.C.S., F.I.C., F.R.S., were elected to honorary membership of the Society at the annual meeting on 7th April, 1948.

During the year nine general monthly meetings were held, at which the average attendance was 49.   Thirty-nine papers were accepted for reading and publication by the Society, an increase of four from the previous year.

At the annual and general monthly meeting of 7th April, 1948, the Acting President, Dr. F. Lions, welcomed Professor Griffith Taylor, of the University of Toronto, Canada, formerly of Sydney University.   Professor Taylor gave an address describing the application of geography, geology and physiography to national planning.

The Council decided to devote portion of the time of general meetings to " Notes, Exhibits and Questions ".   This seems to have met with success, and the following questions have been answered :

4th August :

>   " There is evidence that ice ages have occurred simultaneously in both hemispheres of the world—what is the evidence of this ? "   Answered by Dr. G. D. Osborne.
>
>   " What is a Transcendental Number ? "   Answered by Mr. W. B. Smith-White.
>
>   " What are Cosmic Rays ? "   Answered by Dr. R. E. B. Makinson.

6th October :

>   " Why are there black and white races ? "   Answered by Professor A. P. Elkin.
>
>   " Why does the moon always turn the same face towards the earth ? "   Answered by Mr. Harley Wood.

1st December :

>   " What is the principle of the electron microscope ? "   Answered by Mr. R. L. Werner.
>
>   " What was the cause of the change of longitude of Sydney Observatory amounting to some 166 yards in about the year 1932, as indicated by certain one-inch military maps ? "   Answered by Mr. Harley Wood.

Exhibits discussed were :

5th May :

>   " Bouncing Putty ", by Dr. D. P. Mellor.

3rd June :

>   " Enlarged photographs of the Second Positive Spectrum of Nitrogen, showing some features of interest ", by Professor O. U. Vonwiller and Miss D. P. Tarrant.

A symposium on the " Education of a Scientist " was held at the general monthly meeting on 1st September, the following addresses being given :

" Science in Secondary Education ", by Mr. J. B. Thornton.

" The Teaching of Science in the Universities ", by Professor N. A. Burges.

" The Scientist and Scientific Method ", by Professor K. E. Bullen.

The topic stimulated a deal of discussion, which was continued by other speakers at the next general meeting.

Addresses commemorating great scientists and important scientific events were given at the general monthly meeting on 3rd November :

" Simon Stevin " (Stevinus), by Mr. H. H. Thorne.

" Berzelius ", by Mr. J. B. Thornton.

" Important Events in the History of Public Health ", by Professor Harvey Sutton.

In continuance of its programme of popular education as to atomic energy, the Society made arrangements with the University Extension Board for the delivery of a series of lectures on atomic physics during July :

" The Atom and Radioactivity ", by Dr. D. P. Mellor.

" Artificial Transformations and Nuclear Fission ", by Dr. R. E. B. Makinson.

" Atomic Physics and Human Welfare ", by Dr. F. Lions.

" International Control of Atomic Energy ", by Dr. G. H. Briggs.

Four Popular Science Lectures were delivered during the year, and much appreciated by members of the Society and the public :

20th May : " The Struggle between Fungi and Roots ", by Professor N. A. Burges.

17th June : " Plant Growth Regulators or Hormones ", by Dr. C. J. Magee.

16th September : " The Making of an Australian—A Study in Migration ", by Mrs. C. Kelly.

21st October : " Weights and Measures ", by Mr. N. A. Esserman.

A visit to the National Standards and Radiophysics Laboratories on 30th July was arranged through the courtesy of the C.S.I.R. The opportunity to see the work in progress in these laboratories was appreciated by members.

The Annual Dinner of the Society was held at the Sydney University Union on 31st March, 1949. There were present 98 members and friends.

The Section of Geology, whose chairman was Mr. C. St. J. Mulholland and honorary secretary Mr. R. O. Chalmers, held six meetings during the year, at which the average attendance was fourteen members and six visitors. The activities were :

16th April : Address by Mr. F. N. Hanlon.

21st May : Notes and Exhibits by Miss F. Quodling and Messrs. N. C. Stevens, C. St. J. Mulholland, H. O. Fletcher and R. O. Chalmers.

23rd July : Exhibit by Mrs. K. Sherrard and an address by Dr. L. E. Koch.

27th August : Address by Dr. J. A. Dulhunty.

17th September : Address by Dr. G. D. Osborne and Mr. P. B. Andrews.

19th November : Address by Dr. L. E. Koch.

The Council of the Society held ten ordinary meetings and one special meeting during the year, at which the average attendance was 13. The special meeting of the Council was held to discuss the " Freedom of Science ". It was resolved that at the time no action beyond remaining vigilant appeared desirable, but a motion defining the Council's attitude was recorded in the minute book.

The Council has decided that in future the Annual Report, Financial Statement and List of Members will be published in Part I of the Journal, and that the abstract of proceedings of meetings will be omitted. This will effect more prompt publication of the reports and eliminate some duplication.

Professor O. U. Vonwiller and the Rev. D. J. K. O'Connell were given leave for periods of travel abroad. Among other activities, they represented Australian Science at the Zurich meeting of the International Astronomical Union. Professor Vonwiller represented the Society at the celebration in Sweden of the one hundredth anniversary of the death of Jacob Berzelius. Mr. W. B. Smith-White was elected to the office of Honorary Editorial Secretary rendered vacant by the resignation of Professor Vonwiller.

The President, Dr. R. L. Aston, has represented the Royal Societies of Australia on the National Co-operating Body in Natural Sciences of UNESCO. At the A.N.Z.A.A.S. Conference, January, 1949, at Hobart, the Society was represented by Drs. R. L. Aston, A. Bolliger and C. J. Magee. At the Seventh Pacific Science Congress, which was held in New Zealand, February, 1949, the Society was represented by Dr. Dorothy Carroll.

Dr. A. B. Walkom was one of Australia's representatives at the General Assembly of UNESCO at Beirut, and was president of the Hobart meeting of the Australian and New Zealand Association for the Advancement of Science in January, 1949.

Professor K. E. Bullen has been elected as a Fellow of the Royal Society.

On Science House Management Committee the Society was represented by Messrs. H. O. Fletcher and F. R. Morrison, with substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

Science House Extension Committee has been working on the proposals for the eventual extension of Science House to York Street North, the representatives of the Royal Society of New South Wales being Drs. A. Bolliger and R. L. Aston.

The Clarke Memorial Lecture for 1948 was delivered by Sir Douglas Mawson, O.B.E., D.Sc., F.R.S., on 15th July, the title being " The Sedimentary Succession of the Bibliando Dome : Record of a Prolonged Proterozoic Ice Age ".

The Liversidge Research Lecture for 1948 was delivered by Professor Ian Lauder, M.Sc., Ph.D., on 19th August, on " Some Recent Work on the Separation and Use of Stable Isotopes ".

The Clarke Memorial Medal for 1948 was awarded to Dr. Arthur B. Walkom, Director, Australian Museum, Sydney, in recognition of his contributions to natural science, and particularly for researches in paleobotany.

The Clarke Memorial Medal for 1949 was awarded to the Rev. H. Montague Rupp for his work on Australian orchids.

The Royal Society's Medal was awarded to Professor W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C., F.L.S., in recognition of his valuable researches in the field of agriculture.

The James Cook Medal was awarded to Professor Bernado A. Houssay, of the Instituto d Biologia y Medicina Experimental, Buenos Aires, Argentina, for his distinguished work for science and human welfare in the southern hemisphere, particularly through his contributions to endocrine research.

The Edgeworth David Medal, which is for Australian research workers under thirty-five years of age, was awarded for the first time. It was decided to make a joint award to Mr. R. G. Giovanelli, M.Sc., for his work in astrophysics, and Mr. E. Ritchie, M.Sc., for his work in organic chemistry.

The initiation of the James Cook Medal, in 1948, and the Edgeworth David Medal completes the scheme of the Society's awards which has been envisaged in recent years.

During the year several scientists from overseas visited the Society's rooms and were entertained by the President. Among these were :

Sir Harold Hartley, now Chairman of the British Overseas Airways Corporation (23rd November, 1948).

Sir Henry Tizard, who visited Australia at the invitation of the Commonwealth Government to advise on defence research (8th December, 1948).

Dr. Wang Ghing-Hsi, senior member of the Natural Sciences Department, UNESCO Secretariat, Paris (28th February, 1949).

Drs. A. Sison, P. Valenzuela and J. M. Feliciano, who were members of a party of Philipino scientists returning from the Seventh Pacific Science Congress in New Zealand (14th February, 1949).

Dr. S. Krishna, Lt.-Col. M. L. Ahuja, Dr. B. P. Pal and Mr. V. P. Sondhi, who were members of an Indian scientific delegation visiting Australia at the invitation of the Commonwealth Government (28th March, 1949).

The financial position of the Society, as disclosed by the annual audit, reveals the difficulties which in these years beset institutions whose income tends to remain steady but whose expenditure continues to increase obstinately despite efforts at economy which, if the tendency continues, may eventually affect the efficiency of the Society's work. The most serious example of rising costs for us is in the cost of printing the Journal and Proceedings, which in 1947 was increased from £13 to £16 per forme of 16 pages ; we are now faced with an increase to £32.

The Royal Society's share of the profits of Science House for the year was £390 18s. 6d.

The grant from the Government of New South Wales of £400 has been received. The continued interest of the Government in the work of our Society is much appreciated.

The Library. The amount of £58 6s. 3d. has been spent on the purchase of periodicals, and £121 11s. 3d. on binding, the increased expenditure on binding being due to shortage of bookbinding materials in 1947-1948.

Exchange of publications is maintained with 406 societies and institutions, an increase of 19 over the previous year.

The number of accessions entered in the catalogue during the year ended 28th February, 1949, was 2,501 parts of periodicals.

The Society sold its set of the *Journal of the Royal Asiatic Society of Great Britain and Ireland* to the Library, the Parliament of the Commonwealth, for the sum of £222 12s. 6d. Also, incomplete sets of medical journals were sold to Stechert-Hafner, Inc., of New York, and realized the sum of £202 5s. 11d.

Among the institutions which made use of our library through the inter-library borrowing scheme were : The University of Sydney, Department of Health, University of Queensland, Commonwealth Observatory, C.S.I.R. Food Preservation, Linnean Society of N.S.W., Forestry Commission, C.S.I.R. Plant Industry, National Standards Laboratories, M.W.S. and D. Board, McMaster Laboratory, Taubman's Paints, Elliotts and Australian Drug Co. Ltd., A.W.A. Ltd., C.S.I.R. Industrial Chemistry, Department of Agriculture, Defence Research Laboratories, Water Conservation and Irrigation Commission, Australian Paper Mills, Sydney Technical College, the University of Melbourne, Colonial Sugar Refining Co. Ltd., C.S.I.R. Aeronautics, Standards Association of Australia, C.S.I.R. Coal Survey, Sydney Grammar School, the Australian Museum, Institute of Engineers, James Hardie & Co.

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R. L. ASTON,
President.

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THE ROYAL SOCIETY OF NEW SOUTH WALES.
BALANCE SHEET AS AT 28th FEBRUARY, 1949.

LIABILITIES.

1948. £		1949. £ s. d.	£ s. d.
189	Accrued Expenses		141 5 9
25	Subscriptions Paid in Advance		26 5 0
102	Life Members' Subscriptions—Amount carried forward		90 0 0
200	James Cook and Edgeworth David Medals— Amount carried forward		—
	Trust and Monograph Capital Funds (detailed below)—		
	Clarke Memorial	1,960 4 7	
	Walter Burfitt Prize	1,055 17 5	
	Liversidge Bequest	707 10 3	
7,173	Monograph Capital Fund	3,520 18 4	7,244 10 7
25,877	ACCUMULATED FUNDS		26,081 18 2
(902)	Contingent Liability—In connection with tenancies of the Australian National Research Council and the Pharmaceutical Society of N.S.W.— Maximum Liability £901 16s. 8d.		
£33,566			£33,583 19 6

ASSETS.

1948. £		1949. £ s. d.	£ s. d.
596	Cash at Bank and in Hand		439 14 3
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—		
	Held for—		
	Clarke Memorial Fund	1,800 0 0	
	Walter Burfitt Prize Fund	1,000 0 0	
	Liversidge Bequest	700 0 0	
	Monograph Capital Fund	3,000 0 0	
10,860	General Purposes	4,660 0 0	11,160 0 0
161	Prepayment		24 2 9
	Debtors for Subscriptions	85 5 0	
	Deduct Reserve for Bad Debts	85 5 0	
14,715	Science House—One-third Capital Cost		14,745 18 6
6,800	Library—At Valuation		6,800 0 0
396	Furniture—At Cost—*less* Depreciation		379 0 0
29	Pictures—At Cost—*less* Depreciation		27 4 0
9	Lantern—At Cost—*less* Depreciation		8 0 0
£33,566			£33,583 19 6

TRUST AND MONOGRAPH CAPITAL FUNDS.

	Clarke Memorial.			Walter Burfitt Prize.			Liversidge Bequest.			Monograph Capital Fund.		
	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
Capital at 29th February, 1948 ..	1,800	0	0	1,000	0	0	700	0	0	3,000	0	0
Revenue—												
Balance at 29th February, 1948	128	3	8	97	7	10	25	15	0	421	13	4
Interest for twelve months ..	64	13	11	34	15	0	25	15	0	99	5	0
	192	17	7	132	2	10	51	10	0	520	18	4
Deduct Expenditure ..	32	13	0	76	5	5	43	19	9	—		
Balance at 28th February, 1949 ..	£160	4	7	£55	17	5	£7	10	3	£520	18	4

ACCUMULATED FUNDS.

		£	s.	d.
Balance at 29th February, 1948		25,877	0	11
Add—				
Surplus for twelve months (as shown by Income and Expenditure Account)	£227 10 6			
Decrease in Reserve for Bad Debts	32 7 0			
		259	17	6
		26,136	18	5
Less—				
Amount written off *re* James Cook and Edgeworth David Medals	4 12 0			
Bad Debts written off	50 8 3			
		55	0	3
		£26,081	18	2

The above Balance Sheet has been prepared from the Books of Account, Accounts and Vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1949, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 24th March, 1949.

INCOME AND EXPENDITURE ACCOUNT.
1st March, 1948, to 28th February, 1949.

1947-8. £		1948-9. £ s. d.	£ s. d.
507	To Printing and Binding Journal—Vol. 81	639 13 4	
362	„ Salaries	467 15 1	
150	„ Library—Purchases and Binding	133 6 3	
90	„ Printing—General	103 9 2	
127	„ Miscellaneous	96 11 5	
95	„ Postage and Telegrams	74 0 10	
46	„ Rent—Science House Management Committee ..	54 18 5	
37	„ Cleaning	37 0 0	
23	„ Depreciation	22 16 7	
19	„ Telephone	22 3 7	
15	„ Insurance	23 11 0	
19	„ Audit..	18 18 0	
12	„ Electricity	8 18 2	
18	„ Repairs	1 19 6	
	„ Reprints—		
	Expenditure £153 18 2		
	Less Received 97 9 0		
116		56 9 2	
	„ Annual Dinner—		
	Expenditure £88 13 6		
	Less Received 49 16 0		
21		38 17 6	
31	„ Conversazione	—	
1,688			1,800 8 0
—	„ Surplus for Twelve Months		227 10 6
£1,688			£2,027 18 6

1947-8. £		1948-9. £ s. d.
557	By Membership Subscriptions	586 8 6
400	„ Government Subsidy	400 0 0
482	„ Science House—Share of Surplus	390 18 6
157	„ Interest on General Investments	155 12 1
—	„ Proceeds Sale of Old Library Books	477 18 7
—	„ Other Receipts	5 0 10
10	„ Proportion of Life Members' Subscriptions	12 0 0
82	„ Deficit for Twelve Months	—
£1,688		£2,027 18 6

Obituary.

ERNEST CLAYTON ANDREWS died July 1st, 1948. He was born in 1870 and had occupied a distinguished position in Australian Science for many years. He became a member of the Royal Society of New South Wales in 1909 and was a member of its Council from 1917 to 1932 except in 1919 and in 1927, during the latter of which he was invited to the United States of America to deliver the Silliman Lectures at Yale University. He was president of the Society in 1921 and was awarded the Clarke Memorial Medal in 1928 and the Clarke Memorial Lectureship in 1942.

Andrews was a graduate of the School of Geology of Sydney University, under Professor David, and joined the Geological Survey of New South Wales in 1899, becoming Government Geologist in 1920. His many published papers, twelve of them in the Journal and Proceedings of the Society, show a grasp of a wide variety of geological subjects, but reveal his special insight into the principles governing the evolution of physiographic features and their relation to geological structure. His work in this field in New South Wales may be said to have laid the foundation for all later researches of similar character. In the sphere of economic geology he was equally a master, and his rare geological acumen is displayed in the monumental work on the Broken Hill lode. His studies of the distribution and evolution of floras in Australia and the Pacific Islands form a contribution of high and lasting merit.

Besides his work for our Society, Andrews interested himself widely in the administration of Australian Science. Among the organisations in which he was prominent were the Linnean Society of New South Wales, of which he was president in 1937 ; the Australian and New Zealand Association for the Advancement of Science, Honorary General Secretary 1922 to 1926 and President in 1930 ; the Australian National Research Council ; and the Australian Institution of Mining and Metallurgy, President 1929. On a number of occasions he represented Australian Science at important international congresses.

Andrews received many honours besides those already mentioned, among which were honorary membership of the Washington Academy of Sciences and the Geological Society of America ; honorary fellowship of the Royal Society of New Zealand ; the Mueller Medal of the Australian and New Zealand Association for the Advancement of Science (1946) ; the Lyell Medal of the Geological Society of London (1931) ; and the David Syme Prize and Medal of the University of Melbourne. Through it all he remained a deeply serious and generous worker among his fellow scientists, among whom he was as much esteemed for his personal qualities as he was respected for his scientific attainments.

GEORGE FREDERICK BIRKS died May 4th, 1948. He was 82 years of age and had been a member of the Society since 1923. He was a member of the party which went to Paraguay under the leadership of William Lane to found a socialist colony. After he returned to Australia he entered upon a business career, later becoming a director of several undertakings and chairman of directors of Potter and Birks, Pty., Ltd., a firm of manufacturing chemists which was founded by him. He was much interested in the Rotary movement and was a World Vice-President of the Rotary International. He was also a devoted worker for crippled children, and the Activity School at the Royal Alexandra Hospital for Children is named after him.

ERNEST NORMAN McKIE died May 19th, 1948. He was born at Guyra, New South Wales, in 1882, and spent most of his life around the New England district.

He at first intended to take up a business career and worked with the Commercial Banking Company of Sydney. Later he resigned to enter St. Andrew's College, Sydney University, from which he graduated as Bachelor of Arts in 1906. He completed the theological course in 1908 and took his first church appointment at Manilla, whence he moved to Bendemeer in 1909 and Guyra in 1912. He served as Moderator of the General Assembly of the Presbyterian Church in 1938.

Mr. McKie was an amateur botanist of distinction and had a detailed knowledge of the eucalypts and native grasses of the New England district. His knowledge and help were always available to research workers visiting the district. Beside his interest in botany he took an active part in movements to improve the standard of agriculture in his district, being the first secretary of the local branch of the New South Wales Agricultural Bureau, and for many years associated himself with the fostering of modern trends in agricultural work.

He was a member of the Australian Institute of Agricultural Science, the Linnean Society of New South Wales, to the Journal of which he contributed, and since 1932 of the Royal Society of New South Wales.

EDWARD MONTAGUE WELLISH, M.A., Emeritus Professor of Mathematics of University of Sydney, died after a short illness at his home in Roseville in July, 1948.

He entered the University in 1900 from Fort Street School after a brilliant pass at the Senior Examination in December, 1899, being equal with another student for the John West and Grahame Medals for general proficiency. He attended the evening classes, his guide in mathematics being the late Assistant Professor A. Newham. He graduated with first-class honours and the University Medal in Mathematics. He and Professor C. E. Weatherburn were awarded the University Medal for Mathematics for the M.A. degree in the year 1906.

In 1907 he was awarded the first Graduate Barker Scholarship and entered Emmanue College, Cambridge, in October of that year. He commenced research in the Cavendish Laboratory under Sir J. J. Thomson. His research was on the theory of ionisation of gases, his chief papers during this period being " The Laws of Mobility and Diffusion of Ions formed in Gaseous Media ", *Proceedings of the Cambridge Philosophical Society*, November, 1908 ; and " The Mobilities of the Ions Produced by Röntgen Rays in Gases and Vapours ", *Transactions of the Royal Society of London*, January, 1909 ; and " The Passage of Electricity through Gaseous Mixtures ", *Proceedings of the Royal Society of London*, June, 1909.

Emmanuel College awarded him a special scholarship and a little later the excellency of his work was emphasised by the award of the Clerk Maxwell Studentship. After graduating B.A. (Research) at Cambridge, Professor Wellish accepted the post of Assistant Professor at Yale University, U.S.A. In 1913 he published in the *Philosophical Magazine* " Experiments on Columnar Ionisation " and in the *American Journal of Science* he published two papers, " The Mobilities of Ions in Air " and " The Motion of Ions and Electrons through Gases ".

He returned to Sydney in 1916 and was appointed to a lectureship in the Department of Mathematics and in 1926 he was given the status of Associate Professor of Applied Mathematics. His time for research in Physics was naturally restricted, his next papers appearing in 1924 and 1931, when he published " Photo-electrons and Negative Ions " in the *Proceedings of the Royal Society of London*.

During the nine years when Professors Carslaw and Room were absent from the Department of Mathematics, Professor Wellish was in charge. He retired in 1946, but to the regret of all his friends his health improved only slightly.

Professor Wellish was outstanding in his research, his lecture work and his administrative work. He rendered signal service on the Board of Secondary School Studies. As chief examiner in Mathematics for the Leaving Certificate Examination, he was always sympathetic to school teachers and their problems. His colleagues will always remember his consideration and kindness.

A CONTRIBUTION TO THE STRATIGRAPHY AND PHYSIOGRAPHY OF THE GLOUCESTER DISTRICT, N.S.W.

By P. B. ANDREWS, B.Sc.,

Teaching Fellow in Geology, University of Sydney.

With one text-figure.

I. INTRODUCTION.

·· In a recent paper (Osborne and Andrews, 1948) the geological structure of the northern end of the Stroud-Gloucester Trough was discussed. A full account of previous investigations and a geological map of the area were included in that work. The present paper deals with some aspects of the stratigraphy and physiography of the same area. The major contributions to these subjects have been those of Sussmilch (1921) and Voisey (1940), who have discussed the stratigraphy of part of the area in considerable detail. Carey and Browne (1938) and Voisey (1945) have also discussed the Carboniferous succession at Gloucester and have correlated it with those of other areas. The following notes are intended primarily to extend the work of these investigators, particularly to the areas immediately to the south and east which have an important bearing on the final elucidation of the geology of this interesting district.

II. STRATIGRAPHY.

(a) Carboniferous.

Sussmilch (1921) described a section across the Carboniferous strata on the west side of the Gloucester Trough in the neighbourhood of Barrington village and divided the sequence into the marine Burindi Series and the overlying terrestrial Kuttung Series. Carey and Browne (1938) further subdivided the Burindi Series into lower and upper sections, the Upper Burindi Series being the marine equivalent of the terrestrial Lower Kuttung Series of the Hunter River type area. Voisey (1940) described further sections from the same locality.

The recognition of a large fault separating the Devonian and Lower Burindi strata on the western side of the Trough (Osborne and Andrews, 1948) has confirmed the fact that the base of the Burindi Series is not exposed in these sections. The conglomerates outcropping on the Giro and Copeland Roads which are mentioned by Sussmilch and Voisey appear, however, to be close to the base of the series. A greater development of these conglomerates occurs

on the western side of the Barrington River on the " Manchester " Road, and here the following section was measured in descending order :

						Feet
Conglomerate and tuff	..	..	..	..	..	220
Tuff ..	..	..	..	..	..	165
Mudstones ..	..	..	..	..	..	10
Tuff and tuffaceous conglomerate		..	..	..	..	35
Tuffaceous conglomerate and mudstones			..	..	..	120
Tuff ..	..	..	..	..	..	15
Coarse conglomerate	..	..	..	..	..	60
Tuff ..	..	..	..	..	..	30
Tuffaceous conglomerate		..	..	..	..	70
Tuffs and mudstones	..	..	..	..	..	85
Tuff ..	..	..	..	..	..	50
Conglomerate	..	..	..	..	..	15
Tuffs and mudstones	..	..	..	..	..	85
Conglomerate	..	..	..	..	..	25
Tuffs and mudstones	..	..	..	..	..	80
Total	..	..	..	..	..	1,065

The lowest beds in this sequence are separated by the Manchester Fault from Devonian rocks which outcrop on the flank of Mechanic's Mountain a short distance to the east. Figure 1 shows a columnar section of the Carboniferous strata in this neighbourhood and includes a revised estimate of the upper part of the Carboniferous sequence for the western side of the Stroud-Gloucester Trough.

The series which is shown in Figure 1, and which represents essentially the sections measured by previous workers, can be traced from the Bowman Road Fault, about 2½ miles west of Gloucester, westwards to Barrington village, and thence southward to the Rawdon Vale Road in the vicinity of Cut Hill, where the beds appear to be cut off by an East-West fault.

Work in the area between the Rawdon Vale Road and Spring Creek on the western side of the Trough, and also on the eastern side between the Gloucester-Taree road and Ward's River, has shown, however, that this type section is not developed in any other part of the Gloucester-Stratford district, and none of the datum beds which have been referred to have been located elsewhere in the area.

Owing to the extensive faulting which has taken place, it was found impossible to measure a complete section of the Carboniferous Series on the eastern side of the Trough. Strata of Lower Burindi age outcrop in the country immediately to the south of the Gloucester-Krambach road from a point near the junction of the Mograni Creek road, east at least as far as Gangat, being cut off by faults from Devonian strata to the north and Upper Kuttung and Upper Burindi rocks to the south. These beds consist of mudstones and tuffs dipping steeply to the north. In Brushy Cutting near Gangat a thick series of greenish-grey friable mudstones with subordinate thin bands of tuff is exposed along the road. These beds closely resemble those of the Lower Burindi Series on the west side of the Trough. No fossils have been found in them.

An approximate section of the Upper Burindi and Upper Kuttung rocks on the eastern side of the Trough was measured from Mograni Creek School in a westerly direction. This revealed a total thickness of about 7,400 feet for the Upper Burindi Series, consisting essentially of felspathic and pebbly tuffs and mudstones. These beds are very similar to those of the Upper Burindi Series

on the western side of the Trough, but no fossils were found in them. Over much of this area the beds are dipping vertically, and it is probable that some strike faulting has occurred, thus accounting for the very great thickness measured for the series.

About halfway up in this section is a flow, about 20 feet thick, of green dacitic pitchstone which was traced along its strike for about 1¼ miles but lenses out. Under the microscope the groundmass of this rock is seen to be partly glassy, but is crowded with microlites. A few corroded phenocrysts of quartz are scattered through the rock, and clusters of oligoclase phenocrysts are also present. This may possibly be correlated with a very similar flow which outcrops for a short distance on the ridge to the south of the Rawdon Vale road, where it crosses Cut Hill, where it immediately underlies the topmost flow of quartz-keratophyre in the Upper Burindi sequence.

The top of the first main ridge in the Mograni section is composed of a coarse tuffaceous conglomerate which was considered to be the basal bed of the Upper Kuttung Series, the overlying beds consisting almost entirely of pebbly tuffs and conglomerates in which some obscure plant remains were found. Farther to the south Upper Burindi strata outcrop along the Waukivory Road, and here consist of mudstones and light-coloured coarse felspathic tuffs. Marine fossils were found in Portion 211, A. A. Coy's Grant, close to the road, in a locality mentioned by Voisey (1940). These were not sufficiently well preserved for identification, but included pelecypods and a small gastropod. On the ridge between this point and Phillip's Creek a bed of coarse tuff was found which contains crinoid stems, but most of the considerable thickness of pebbly tuffs and mudstones are apparently unfossiliferous. The presence of the East Stratford Fault, which separates these beds from the Upper Kuttung Series, prevents the determination of the exact position in the sequence of the fossiliferous horizons.

The rugged country at the head of Dog Trap Creek and Ward's River consists of a great thickness of apparently unfossiliferous tuffs and tuffaceous conglomerates with subordinate mudstones. The ridge on which is situated Craven Trigonometrical Station is formed of one of the beds of coarse tuffaceous conglomerate. These sedi-
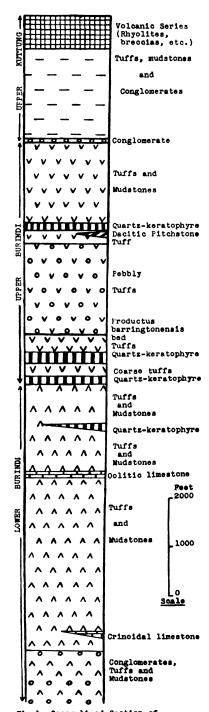

Fig.1. Generalised Section of Carboniferous Strata on western side of Stroud-Gloucester Trough.

ments are again very similar to those of the Upper Burindi Series on the western side and are provisionally correlated with them. In this neighbourhood the strata dip to the east at angles of about 70 degrees and are cut off on the west by the East Stratford Fault.

The steep ridges on the western side of the Stroud-Gloucester Trough, south of the Rawdon Vale road, also consist almost entirely of pebbly tuffs. However, a flow of rhyolite forms the highest part of the ridge between Cut Hill Creek and the upper Avon River. South of the Avon River the crest of the Faulkland Range is formed of another thin flow of acid lava, in this case a light grey, wholly glassy rock with numerous veinlets of quartz. Here, however, the associated sediments, which include dark-coloured cherts and a few thin beds of carbonaceous shale, appear to belong to the Upper Kuttung Series. Pebbly tuffs and mudstones which outcrop on the western flank of the Faulklands Range are believed to be of Upper Burindi age, but no detailed work was carried out in this locality.

Carey and Browne (1938) suggested that the type section of the Upper Burindi Series on the western side of the Gloucester Buckets Range was a predominantly terrestrial sequence with thin marine intercalations. Voisey (1945) considers that the whole of the Upper Burindi Series is marine. A careful study of these beds has shown that fragments of marine fossils are widely distributed through the series, but it is possible that there are some terrestrial sediments interbedded in an essentially marine sequence. It must be emphasized that the whole facies is indicative of shore-line conditions.

The almost complete absence of marine fossils from the corresponding beds on the eastern side of the Trough may indicate that this particular area was one of predominantly terrestrial deposition, the same types of tuffs and pebbly beds being present as in the marine series on the western side. It is also significant that no marine fossils have been found in similar beds on the western side farther south than the Rawdon Vale road.

Thus it is probable that much of the strata indicated on the previously published map (Osborne and Andrews, 1948) as belonging to the Upper Burindi Series is, in fact, of terrestrial origin. As the distinction is purely one of facies and not of age it has been considered advantageous to classify all these rocks under a single head.

The most notable feature of the Upper Kuttung Series in the Gloucester-Stratford district is the great development of volcanic rocks. These have been discussed by Sussmilch (1921) under the name of the "Gloucester Rhyolites", but Voisey (1945) has pointed out that the greater part of the volcanic series consists of fragmental material. This is particularly the case on the eastern side of the Stroud-Gloucester Trough where these strata attain their greatest development. The total thickness of the volcanic series in the neighbourhood of Mograni Mountain is about 3,000 feet. No attempt has been made to map individual flows, of which there are a large number, but many different varieties have been collected. A great deal of brecciated material is present, the fragments consisting largely of banded rhyolites and tuffs of several kinds. Many of the lavas exhibit large vughs and veins filled with chalcedony, and it is interesting to note that this is also the case at Pokolbin, where lavas occur which are almost identical chemically with some of those of the Gloucester Buckets Range. The lavas range in composition from rhyolites to andesites, blue dacites showing strong flow structure being particularly well developed in the vicinity of Oaky Creek Falls.

The Upper Kuttung Series to the west of Stratford and Craven consists almost entirely of tuffs and tuffaceous conglomerates, and the typical volcanic sequence is not developed, although it still appears in the ranges on the east

side of the valley. At the head of the Upper Avon road, pink and purplish volcanic breccias outcrop, but these are of an entirely different type from the brecciated lavas of Mograni Mountain.

(b) Permian.

Rocks of Permian age occupy the central part of the Stroud-Gloucester Trough and consist of conglomerates, grits, sandstones, shales and coal seams. These beds have been assumed to belong to the Upper Coal Measures (Sussmilch, 1921 ; Voisey, 1940) but no direct correlation can be made as they are isolated from the main coal basin of the Hunter River Valley and a correlation based purely on lithological similarities cannot therefore be accepted.

Owing to the presence of much minor folding and variations in dip, and to the paucity of good outcrops, the thickness of the Coal Measures cannot be accurately measured, but in the neighbourhood of Gloucester there is a total thickness of at least 1,900 feet. No clearly defined junction between these beds and the underlying Upper Kuttung Series has yet been found, owing to the characteristic talus slopes which everywhere mark the boundary of the volcanic series, but in a track cutting close to the Barrington River near Kiaora Crossing, and in the railway cutting immediately north of the bridge over the Avon River, the two series appear to be separated by an erosional disconformity, the Permian rocks occupying hollows in the surface of the Upper Kuttung lavas. The basal bed of the Permian sequence wherever studied is a coarse conglomerate containing pebbles of rhyolite and tuff which gives further evidence of a probable erosional break between the two series.

The best exposures of the Coal Measures are to be seen in the railway cuttings between Spring Creek and Craven, in the southern part of the area under discussion. A large number of outcrops of coal seams appear in these cuttings, but most of the seams are very thin. These beds show many minor folds and faults (Osborne and Andrews, 1948). In the bed of Coal Creek about one-quarter mile south of Craven Railway Station a section was measured totalling 146 feet of sediments, of which 24 feet is coal, but this is distributed between thirteen distinct seams.

To the east of Craven, along the Glen road and south at least as far as Stoney Creek, is a faulted outlier of Coal Measures consisting essentially of sandstone and conglomerate. A 14-foot seam of coal is exposed in the bed of Stoney Creek a short distance above its confluence with Ward's River.

III. Physiography.

Sussmilch (1921) briefly discussed the major physiographic features of the Gloucester district and mentioned the contrast between the relatively flat and low-lying valley of the Gloucester, Avon and Ward's Rivers, excavated in soft Permian strata, and the steep country on either side occupied by Carboniferous rocks.

Extensive alluviation of the lower reaches of the Gloucester and Avon Rivers at the northern end of the valley has taken place, and this is probably partly due to the blocking of the Gloucester River immediately above its junction with the Barrington River by a hard bar of Carboniferous lavas which is an extension of the Mograni Range. This would have formed a local base-level for the river. This is confirmed by the presence of a river terrace which is revealed in a road cutting where the river passes on the north side of the town of Gloucester and which is about 40 feet above the present river level.

In the main valley, the divide between the Avon River system flowing northward and the Ward's River system flowing to the south is very low and

irregular.   Ward's River flows out of the ranges on the eastern side in a narrow valley at an average elevation about 100 feet lower than the land immediately to the north, and its tributaries, cutting back in this direction, threaten to capture the headwaters of Swamp Creek which now flows over an almost level plain before joining the Avon River.   In a similar way Spring Creek, which flows into Ward's River from the west, threatens to capture the heads of some of the small creeks which flow northward to the Avon River on the western side of the North Coast Railway.   If these changes were to take place the whole drainage pattern of the Avon River would be reversed.

Sussmilch noted that the main stream channels appear to antedate the present topography, and it may be noted that this also applies to many of the smaller streams, which have cut across hard and weak structures alike.   On the eastern side of the main valley Ward's River, Waukivory Creek, Dog Trap Creek and Mograni Creek all rise in the country to the east of the Mograni Range and have cut steep gorges through it as they flow westward, cutting at right angles across the general trend of the country to do so.   Waukivory Creek flows in a relatively mature valley on the eastern side before plunging into a narrow gorge through the range, which rises to a height of over 1,000 feet on either side.

In the same way the Gloucester River and Gap Creek have cut through the Gloucester Buckets Range on the western side.   The case of Gap Creek is particularly noteworthy, as it rises in low hills within a mile of the Barrington River, but flows eastward by way of a deep and narrow gorge through the Gloucester Buckets into the Gloucester River.

The course of the Barrington River is of great interest.   Between Berrico and Faulklands are a series of entrenched meanders, but at the latter locality the river turns sharply and flows northward, approximately parallel to the strike of the Carboniferous strata.   Where the strike of these rocks swings round to the east in the vicinity of Barrington village the river continues northward for another mile and then turns sharply to the east.   Farther downstream the river flows approximately parallel to the strike of the Devonian strata on the northern bank, but here its course is determined primarily by the presence of the Barrington River Fault.   The reasons for the two abrupt changes of course are difficult to visualize, but that at Faulklands may have been caused by piracy of the head of the old river by a young stream cutting back along the strike from the north, the old river having previously flowed to the east, as is still the case with the Gloucester River.

IV. CONCLUSION.

The above notes are intended primarily to extend the work of previous investigators and to present some aspects of the stratigraphy and physiography of the Gloucester-Stratford district which have not previously been discussed. It is emphasized that the important Carboniferous sequence of the western side of the Stroud-Gloucester Trough, which has been the subject of much discussion is developed only within a comparatively limited area, and in particular is not found on the eastern side of the Trough in the neighbourhood of Gloucester.

V. ACKNOWLEDGEMENTS.

VI. REFERENCES.

Browne, W. R., and Walkom, A. B., 1911.   The Geology of the Eruptive and Associated Rocks of Pokolbin, N.S.W.   THIS JOURNAL, **45**, 379.
Carey, S. W., and Browne, W. R., 1938.   Review of the Carboniferous Stratigraphy, Tectonics and Palæogeography of N.S.W. and Queensland.   THIS JOURNAL, **71**, 591.

Osborne, G. D., 1922. Geology and Petrography of the Clarencetown-Paterson District. Part I. *Proc. Linn. Soc.* **46**, 161.

—————————— 1938. On Some Major Geological Faults North of Raymond Terrace and their Relation to the Structure of the Stroud-Gloucester Trough. THIS JOURNAL, **71**, 385.

Sussmilch, C. A., 1921. The Geology of the Gloucester District of New South Wales. THIS JOURNAL, **55**, 234.

Voisey, A. H., 1940. The Upper Palæozoic Rocks in the Country between the Manning and Karuah Rivers, New South Wales. *Proc. Linn. Soc. N.S.W.*, **65**, 192.

—————————— 1945. Correlation of Some Carboniferous Sections in New South Wales. *Proc. Linn. Soc. N.S.W.*, **70**, 34.

Osborne, G. D., and Andrews, P. B., 1948. Structural Data for the Northern End of the Stroud-Gloucester Trough. THIS JOURNAL, **82**, 202.

THE EFFECT OF DIFFUSIONAL PROCESSES ON THE RATE OF CORROSION.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

LIMITATIONS OF CORROSION TESTS.

Reviews of corrosion test procedure by White (1934), McKay and La Que (1937), La Que and Knapp (1945) and by others have stressed the necessity for a very close standardization of conditions. If measurements of the rate of loss of mass from a metal test piece in a given corrodant liquid are to be any guide to the behaviour of metal members under large-scale conditions, very close attention must be paid to a number of details, such as the depth of immersion, the methods of suspension or support and the conditions of aeration and circulation of the fluid ; as well as to such more obvious factors as the temperature and pH of the corrodant liquid and the presence or absence of other metals forming electro-chemical couples with the test specimen. White, indeed, has emphasized the difficulty in getting reproducible results even with different specimens of the same dimensions, and La Que and Knapp have stressed the necessity for a detailed evaluation of the proposed conditions of application in order that these may be duplicated as closely as possible in the laboratory tests.

The overall reaction of a metal dissolving in an electrolyte to give either a soluble or insoluble ionic product has long been recognized as a complicated one. Many successive physical and chemical operations are involved. Much attention has recently been given to some of these operations, especially those of a more chemical nature, such as interphase ionic transfer, anodic and cathodic polarization, and the effect thereon of inhibitors and accelerators. On the other hand the effect of the transport processes which bring the active depolarizing agent up to the seat of attack and remove therefrom the products of reaction has not received such close attention. It is clear, for example, that in the corrosion of copper by acetic acid in which the reaction is maintained by cathodic depolarization produced by dissolved oxygen, the maintenance of the chemical attack is dependent on the continuity of the supply of oxygen to the cathodic areas ; and it is conceivable that, under certain conditions, the rate of diffusion of oxygen might become a rate determining factor.

The conception of a set of physical transport phenomena entering into the final determination of the rate of chemical attack by a corrodant liquid is one which has been paralleled in recent years in other fields of applied chemistry. Thus Damköhler (1936), Edgeworth Johnstone (1939), Laupichler (1938), Hurt (1945) and Bosworth (1947) have all discussed the effect of such factors as the flow of heat and flow of reactants and resultants on the course of chemical reactions in small and large scale reactors. Further, Agar and Hoar (1948) have discussed the effect of a change of scale on an electrochemical system and have concluded that the rate controlling step for a large scale system is not necessarily the same as for a small scale system under otherwise identical chemical and physical conditions.

VARIABLES OF THE TRANSPORT PROCESS.

It appears desirable, therefore, to examine the process of corrosion with a view to enumerating and, if possible, devising methods of measuring the factors which are concerned in the transport of matter to and from the corroding surface. In this object there is one obvious mode of attack. Recently a number of authors (Sutton, 1934 ; Powell and Griffiths, 1939 ; Pasquill, 1943 ; and Boelter, Gordon and Griffin, 1946) have traced a degree of parallelism between heat loss and loss of matter by evaporation from geometrically similar bodies. Since it is not unreasonable to expect that matter loss from corroding bodies might also behave similarly, and further since the laws of conduction and convection of heat are particularly well known, the first object of this paper and of the two succeeding papers will be an attempt to trace a degree of parallelism between heat loss and matter loss by corrosion from geometrically similar bodies. This paper will be specifically concerned with transport under stagnant fluid conditions, analogous to the transport of heat in a fluid by thermal conductivity alone.

The corrosion rate q, in mass flow per unit area per unit time, and the corrosion cell e.m.f. E are, clearly, two of the properties with which we will be concerned. The quantity E is the driving force which produces a flow of matter q. While much has been discovered from purely electrochemical measurements concerning the mechanism whereby E produces the matter flow q, we are not here immediately concerned with this subject. We are, however, concerned with the property which might be defined as the overall chemical resistance (or impedance) of the system—that is to say the factor which determines the magnitude of the driving force required to produce a given flow rate. Since various successive reactions are involved in the corrosion process, this overall resistance can presumably be split into a number of series (or parallel) components, one corresponding to each step in the corrosion process ; in much the same way as the flow of heat in a multi-component system can be represented by a number of series (or parallel) thermal resistances. Among the factors contributing components to the overall chemical resistance are the transport processes leading to the removal of the anodic and cathodic products of corrosion from the immediate vicinity of the interface under attack. Removal may be effected by diffusion, turbulent diffusion, or by the convection currents set up either as a result of density changes produced by the solution of heavy metal ions, or from temperature changes. Since the mechanism of removal of the products of reaction controls the degree of polarization, it also controls the magnitude of the electric current across the metal-electrolyte interface and thus the rate of corrosion. The transport processes involved in the removal of matter from the vicinity of the interface bear a formal similarity to those exhibited by the heat loss from a hot body immersed in a fluid. Heat may be carried from such a body by molecular conduction, turbulent conduction, by forced convection if the fluid is stirred, or by natural convection.

Examples of corrosion in which an insoluble phase resulting from chemical reaction consequent to corrosion builds up a barrier to the diffusion process, or those in which the corrosion reaction is maintained by the presence of a bimetallic system providing a permanent cell e.m.f. obviously involve a transport mechanism which is more complicated than that involved in the flow of heat. However, when uniform, or general corrosion alone occurs, it would appear that the transport processes have features in common, and it is this suggested similarity which will be discussed below.
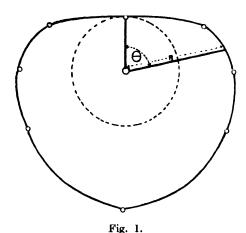
EXPERIMENTAL.

The subjects of experimentation were selected so as to avoid the more complicated types of corrosive attack. The subjects consisted of copper,

certain copper alloys and steels in acetic acid-acetic anhydride mixtures. Commercial acetic acid has a high electrical resistivity of the order $1 \cdot 5 \times 10^{-6}$ ohm-cms., and accordingly bimetallic corrosion is not serious. The acetates are soluble, and thus complications due to the formation of barriers are avoided. Further, experience has shown that these systems do not show the phenomenon of dezincification in which one component of an alloy selectively dissolves. The only type of corrosion is a general attack all over the surface exposed to the acid. Accordingly these systems are particularly suitable for the examination of the influence of convection on the process of corrosion.

The equipment used consisted of a cylindrical body C of the metal under test, 3 cms. in diameter and $1 \cdot 8$ cms. long. One flat face of this body contained a cylindrical hole $1 \cdot 0$ cm. in diameter and $0 \cdot 8$ cm. deep coaxial with the body as a whole. Into this hole there fitted snugly a second cylinder, B, of the same metal, the two top faces being coplanar. These two faces were polished together. Cylinder B was removed and weighed and then placed back in position. The air was pressed out through a hole at the back of C, and this hole was finally closed by means of a screw also of the same metal. A thin film of an acid-proof grease used for lubrication prevented the corrodant from coming into contact with any portion of B other than the front face. This equipment thus permitted a study of the attack on a definite area of a single metal face surrounded on all sides by a surface of the same metal, which thus acted as a guard ring and, by eliminating irregularities in the field of the corrodant at the edges, reduced the geometrical pattern of the flow of matter to and from the face under attack to one in a single dimension.

After subjection to the corrosive conditions for a measured time, cylinder B was removed, the acid-proof grease was dissolved in a volatile solvent and the cylinder dried and weighed.

Fig. 1.

THE EFFECT OF ORIENTATION.

The equipment as described above was first used in a study of the effect of orientation on the rate of corrosion. An iron (mild steel) surface was immersed 4 cms. in a 60/40 acetic acid-acetic anhydride mixture and the rate of corrosion measured at different orientations as the face was turned in a vertical plane through 2π. The results are shown in the form of a vector diagram in Figure 1. In this diagram the r co-ordinate measures the rate of corrosion and the θ co-ordinate the azimuth.

It will be seen from the figure that the rate of loss of matter is a minimum when the corroding surface is facing upwards and a maximum when facing downwards.   Evans and Mears (1934) have already remarked on the flow of heavy metal salt solution under gravity away from all surfaces except those facing vertically upwards.   This flow constitutes a convection current opposite in direction, but essentially similar in nature, to the convection currents surrounding a hot body in a fluid.   Thus it is seen from Figure 1 that the corrosion rate is a maximum when the convection current is most intense and a minimum when there is no convection and when the loss of matter takes place entirely by a " conductive " mechanism.

In taking measurements of the corrosion rate with all transport processes restricted to those of the " conductive " type, it is of importance to be able to estimate the error involved in any slight departure of the surface from the horizontal position—say by an angle θ.   Since the top of Figure 1 is flat, it follows that the error is of the order $q/\cos\theta$ or $q(1+\theta^2)$, where q is the measured rate.   Errors of magnitude sensible in comparison with the random errors usual even in the best corrosion measurements are thus not incurred unless θ is greater than $0\cdot2$ radian or $12°$, which quantity is thus a measure of the tolerance allowed on the orientation.

EFFECT OF VARYING THE DEPTH OF IMMERSION.

The property of thermal conductivity plays a large part in all successful attempts at the co-ordination of experimental determinations on the rate of conductive and convective transfer of heat.   If a similar co-ordination of the effects of convection on the corrosive transfer of matter is to be attempted, it is
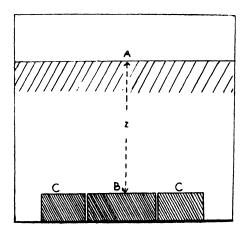

Fig. 2.

important to find that property concerned with the transport processes involved in corrosion which plays the same part as thermal conductivity does to heat flow in fluids.   Such a property could be measured by an adaption of the guard-ring method of measuring thermal conductivity.   If we set up the equipment, described in the section above, horizontally at a distance z below a free surface, we will effectively be concerned with one-dimensional diffusion through a distance z, the depolarizing agent (atmospheric oxygen) having to travel that distance through a stagnant layer of the corrodant liquid.

In Figure 2, let A represent the free surface of the corrodant and B and C respectively the surface under attack and the guard-ring both at a distance z from the free surface and parallel to it.   We are concerned with a flow of matter

from B to the liquid ; the flow, on account of the influence of the guard-ring, being normal to the surface. This flow, the magnitude q of which may be measured by weighing the central cylinder before and after a measured time interval, is stoichiometrically connected with all chemical steps in the corrosion reaction. One of these steps is the " conductive " flow of the depolarizing agent through a distance z. The magnitude of q therefore might be expected to vary with z in the same way as the flow of heat from a geometrically similar hot plate separated from another plate, at a temperature difference θ from the former, by a convectionless thermal conductor of conductivity k_θ. In such a thermal system the heat flow q_θ per unit area per unit time is related to θ by an equation :

$$k_\theta = \frac{q_\theta z}{\theta} .$$

If dq_θ is the heat flow change associated with a change dz in the thickness of the thermal conductor, we have

$$k_\theta = \frac{1}{\theta} \frac{dz}{d(1/q_\theta)} \quad \dots\dots\dots\dots\dots\dots \quad (1)$$

In the mass flow system involved in the corrosion process we may readily measure the change in the rate of corrosion (dq), in units of mass crossing unit area in unit time, produced by a change dz in the length of the path through which the depolarizing agent is conducted. In this system now we may define a corresponding conductivity term k_c by means of an expression analogous to equation (1), viz.

$$k_c = \frac{1}{E} \frac{dz}{d(1/q)} , \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

where by E is to be understood the overall driving force for the corrosion reaction, or the corrosion cell e.m.f.

If for a given system k_c is a constant, or if in other words the system follows a law analogous to Fourier's law, then we expect to get a straight line when the depth z is plotted against the reciprocal of the rate of corrosion $(1/q)$. Experimental data obtained on the guard-ring equipment are represented in Figures 3 and 4, where $1000/q$ is plotted against z for the different systems studied. The experiments were conducted in a thermostat at two different temperatures, namely $20°$ C. and $70°$ C. The $1/q$ versus z lines are straight, but do not pass through the origin. Each system may thus be described by two constants ; the intercepts $1/q_0$ on the $1/q$ axes which incidentally are always positive, and the slopes $\left(\dfrac{dz}{d(1/q)}\right)$, which we shall denote hereunder by the symbol j. We see, therefore, that the process of transport of matter involved in a corrosion reaction taking place under " conductive " conditions involves two properties of the system, j and q_0. The significance of these properties will be discussed below, but first it is desirable to consider the units in which these quantities are to be measured and the magnitude of these properties for typical systems.

<div style="text-align:center">UNITS.</div>

Many problems connected with the transport of matter and of heat which are too complicated for a complete mathematical treatment have been successfully treated by the use of dimensionless quantities. In order to combine the quantities connected with the transport phenomena concerned with corrosion, it is first necessary to use a consistent set of units throughout. The various phenomena involved can be reduced to four fundamental dimensions. Now q the rate of corrosion is, in the technical literature, commonly measured in units

of milligrammes decimetres^{-2} days^{-1}, while E, the corrosion cell e.m.f., is commonly measured in volts. We shall accordingly take for our four fundamental units the quantities, decimetres, milligrammes, days and volts. Thus the quantity j above is to be measured in milligrammes decimetres^{-1} days^{-1}, while k_c is to be measured in milligrammes decimetres^{-1} days^{-1} volts^{-1}.

The units in which the other properties of importance are to be measured will be given later. For convenience this system of units will be referred to as the d.m.d.v. system.

RESULTS.

The experimental results calculated from the lines shown in Figures 3 and 4 are tabulated in Table 1. For each system and temperature studied the two properties j and q_0 are recorded, each of course, in d.m.d.v. units.

TABLE 1.

Metal.	Corrodant.	Temperature.	Slope j Milligrammes dm^{-1}, day^{-1}.	Reciprocal Intercept q_0 Milligrammes dm^{-2}, day^{-1}.
Copper.	Acetic anhydride	20° C.	9·6	51
,,	60/40 acetic acid/acetic anhydride	,,	10·5	125
,,	Glacial acetic acid	,,	13·8	150
,,	50% aqueous acetic acid ..	,,	6·0	97
,,	50/50 acetic acid/benzene ..	,,	195	405
,,	60/40 acetic acid/acetic anhydride	70° C.	190	2000
,,	Glacial acetic acid	,,	710	2000
Brass.	Acetic anhydride	20° C.	1·6	71
,,	60/40 acetic acid/acetic anhydride	,,	6·2	66
,,	50% aqueous acetic acid. ..	,,	3·3	70
Phosphor bronze.	60/40 acetic acid/acetic anhydride	20° C.	18·2	135
,,	Glacial acetic acid	,,	20·0	130
,,	50% aqueous acetic acid ..	,,	16·0	100
,,	Glacial acetic acid	70° C.	660	1050
Mild steel.	60/40 acetic acid/acetic anhydride	20° C.	52·0	1000
,,	Glacial acetic acid	,,	62·0	950

DISCUSSION.

The lines represented on Figures 3 and 4 relating the variation of the rate of corrosion with the depth can be put in the form

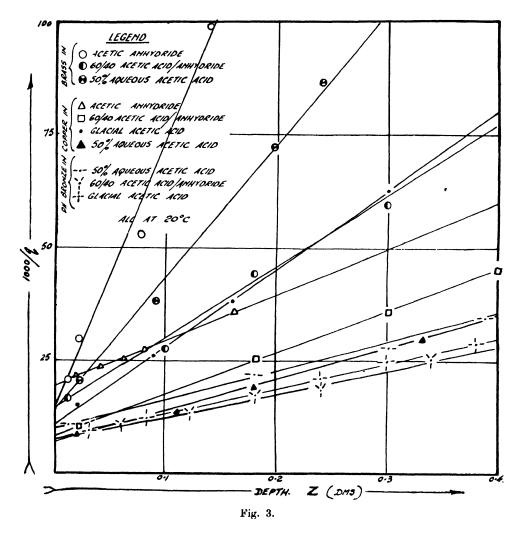$$\frac{1}{q} = \frac{1}{q_0} + \frac{z}{j} \quad \dots\dots\dots\dots\dots\dots\dots\dots (3)$$

A similar expression would have been given for the heat loss across a thermal conductor of various thickness from a hot body, which however is not bare but thermally lagged so that the rate of heat loss can never exceed a certain figure.

The property j is related to the correction conductivity k_c by the expression

$$j = Ek_c \quad \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

and is more convenient than k_c because the quantity E is not directly concerned in corrosion measurements. The quantity j is a measure of the conductivity of the corrodant for the depolarizing agent and is thus a measure of a sensitivity of

the reaction concerned to control through limiting the supply of depolarizing agent.   A reaction giving a small j such as brass in acetic anhydride is strongly dependant on the supply of atmospheric oxygen.

The quantity q_0 is a measure of the rate of corrosion when the depolarizing agent is made instantly available at the surface and is thus a quantity of more direct chemical significance than measures of q under any standard conditions of

Fig. 3.

immersion or aeration.   The ratio E/q_0 is a measure of the resistive force opposing the corrosion process when the effect of all physical factors limiting the supply of the depolarizing agent to the surface have been eliminated.   If we denote this resistance by r, viz.

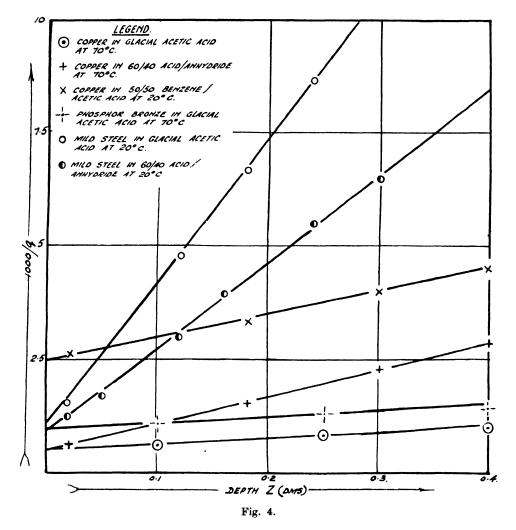$$r = E/q_0 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

We then have, for the net driving force available for maintaining the transport of depolarizing agent to the surface under attack when the specimen is corroding at a rate q,

$$E - qr \text{ or } E(1 - q/q_0) \text{ volts.}$$

This is the factor with which we will be concerned in treating the more complicated phenomena concerned with transport processes involving forced and natural convection.

SUMMARY.

The influence of the processes involving the transport of matter on the rate of corrosion has been studied by means of a circular disc protected by a guard-ring. This device reduced the geometrical nature of the flow of matter to one in a single dimension. The variation of the corrosion rate of such a surface was

Fig. 4.

studied as a function of the orientation of the surface and shown to be a minimum when it faced upwards. It was concluded that convective transfer was absent under these conditions. The corrosion rate, from a horizontal surface facing upwards and protected by an electro-chemical guard-ring, was then studied as a function of the depth of immersion.

The systems studied included copper, copper alloys and steel in acetic acid, acetic anhydride mixtures. Experimental results plotted in the form : reciprocal

of the corrosion rate ($1/q$) versus the depth (z) of immersion give straight lines with positive intercepts on the $1/q$ axis. These intercepts have been interpreted as a measure of the rate of corrosion under such conditions that the depolarizing agent (atmospheric oxygen) is made freely available at the surface. The slopes have been interpreted as a measure of the " conductivity " of the corrodant for the depolarizing agent, a factor which, it is suggested, would be of primary importance in the interpretation of the effect of convection of the rate of corrosion.

REFERENCES.

Agar, J. N., and Hoar, T. P., 1948. *Trans. Farad. Soc.*

Boelter, L. M. K., Gordon, H. S., and Griffen, J. R., 1946. *Ind. Eng. Chem.*, **28**, 596-600.

Bosworth, R. C. L., 1947. THIS JOURNAL, **81**, 15-23 ; *Trans. Farad. Soc.* **43**, 399-406.

Damköhler, G., 1936. *Zeits. Electrochem.*, **42**, 846-862.

Edgeworth Johnstone, R., 1939. *Trans. Inst. Chem. Engrs. (London)*, **17**, 129-136.

Evans, U. R., and Mears, R. B., 1934. *Proc. Roy. Soc.* A **146**, 153-165.

Hurt, D. M., 1943. *Ind. Eng. Chem.*, **35**, 522-528.

La Que, F. L., and Knapp, B. B., 1945. " Corrosion and Material Protection," **2** No. 1, 17-23.

Laupichler, F. G., 1938. *Ind. Eng. Chem.*, **30**, 578-586.

McKay, R. J., and La Que, F. L., 1937. A.S.T.M. Symposium on Corrosion Testing Procedure, 87

Pasquill, F., 1943. *Proc. Roy. Soc.*, A **182**, 75-95.

Powell, R. W., and Griffiths, E., 1939. *Trans. Inst. Chem. Engrs. (London)*, **36**, 125-143.

Sutton, W. G. L., 1934. *Proc. Roy. Soc.*, A **146**, 701-722.

White, A. S., 1934. *Industrial Chemist*, **10**, 98-101.

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THE INFLUENCE OF FORCED CONVECTION ON THE PROCESS OF CORROSION.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

INTRODUCTION.

That the phenomena occurring at the interface between a fluid electrolyte and an electrode, usually solid, can be influenced by the mechanism available for the transport of ions in the fluid has been recognized since the days of Nernst (1904). Nernst introduced the concept of a *diffusion layer* as that of a quiescent fluid zone of definite thickness across which matter may be transferred only by molecular conduction and in which no convection currents occur. The bulk of the fluid outside the diffusion layer is assumed to be so well stirred up by convection as to be effectively at uniform concentration. It then follows that the rate of transfer to the interface is governed by the product of the concentration difference across the diffusion layer, the diffusivity in the layer and the reciprocal of the thickness of the layer. Since the diffusivity is a specific property of the system concerned the diffusion layer thickness is the property which determines the influence of concentration difference on the rate of transfer.

The Nernst concept of a *diffusion layer* has been extended by Levich (1942, 1944, 1947) to that of a *diffusion boundary layer* defined by analogy with the boundary layers of hydrodynamics and of thermal convection. Agar (1947) has used this concept of a diffusion boundary layer treated as a Nernst diffusion layer in order to estimate the influence of the current density on overvoltage, and has applied his figures specifically to the deposition of iodine. His method is based on an assumed analogy between matter flow and heat flow both under conditions of natural convection and the final figures he obtains supports his initial assumptions. He makes no use of the analogy other than that of determining boundary layer thicknesses and associated properties.

In a series of measurements on the rate of transfer of metal ions from solid metal to liquid electrolyte—or measurements of the rate of corrosion of certain metals by acids—under such conditions that all convection currents could reasonably be presumed to have been eliminated, the author (Bosworth, 1949) was led to infer a possible analogy between corrosive matter loss and convective heat loss from a lagged hot body geometrically similar to the one undergoing corrosion. It is clear that if this analogy could further be developed it would yield information on other properties concerned in the transport of matter as well as the diffusion boundary layer thickness. This, and the succeeding paper, will describe attempts to study the behaviour of corroding bodies under regulated conditions of forced and natural convection by the same method as that which has proved so successful in heat transfer problems; namely by the use of dimensionless quantities analogous to the Nusselt, Prandtl, Peclet and Grashof numbers.

THE TABLE OF ANALOGOUS PROPERTIES.

Table 1 below gives, on the left-hand side, a list of the properties and their units used in the treatment of forced and natural convection from a cylindrical

TABLE 1.

Thermal Properties.			Properties Connected with Corrosion.		
Property.	Symbol.	Unit.	Property.	Symbol.	Unit.
Heat Flux	q	cals. cm.$^{-2}$ sec.$^{-1}$.	Corrosion rate	q	mgrms. dm.$^{-2}$ day^{-1}.
Temperature difference	θ	°C.	Limiting corrosion rate	q_0	mgrms. dm.$^{-2}$ day^{-1}.
Transmittance	h	cals. cm.$^{-2}$ sec.$^{-1}$ °C.$^{-1}$	Effective cell e.m.f.	$E(1-q/q_0)$	volts.
Thermal conductivity	k	cals. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$	—	$\dfrac{q}{E(1-q/q_0)}$	mgrms. dm.$^{-2}$ day^{-1} volt^{-1}.
Diameter of hot body	d	cms.	—	$\dfrac{E(1-q/q_0)}{j/E}$	mgrms. dm.$^{-1}$ day^{-1} volt^{-1}.
Length of hot body	l	cms.	Diameter of corroding body	d	dms.
Mass rate of flow	Γ	grms. sec.$^{-1}$.	Length of corroding body	l	dms.
Viscosity	η	poises.	Mass rate of flow	γ	mgrms. day^{-1}.
Acceleration due to gravity	$g(981)$	cms. sec.$^{-2}$.	Viscosity	η	mgrms. dm.$^{-1}$ day^{-1}.
Heat capacity (Const. p)	c_p	cals. grm.$^{-1}$ °C.$^{-1}$.	Acceleration due to gravity	$g(7.32.10^{11})$	dm. day^{-2}.
Density	ρ	grms. cms.$^{-3}$.	Density	ρ	mgrms. litre^{-1}.
Quantity of heat per unit volume.	$c_p\rho\theta$	cals. cm.$^{-3}$.	Quantity of corrodant per unit volume.	C	mgrms. litre^{-1}.
Volumetric heat capacity	$c_p\rho$	cals. cm.$^{-3}$ °C.$^{-1}$.	Quantity of corrodant per unit volume required to change E by unity.	$K=\dfrac{\partial C}{\partial E}$	mgrms. litre^{-1} volt^{-1}.
Coefficient of volumetric expansion	$\beta=\dfrac{1}{\rho}\dfrac{\partial\rho}{\partial\theta}$	°C.$^{-1}$.	—	$\dfrac{1}{\rho}\dfrac{\partial\rho}{\partial C}\dfrac{\partial C}{\partial E}=\dfrac{\xi K}{\rho}$	volt^{-1}.
Thermometric conductivity	$x=\dfrac{k}{c_p\rho}$	cms.^{2} sec.$^{-1}$.	Diffusivity of corrodant	$D_c=\dfrac{j}{EK}$	dm.^{2} day^{-1}.

body.   On the right-hand side the corresponding properties associated with the flow of the depolarizing agent to a corroding body are given with their units and suggested symbols.   The units have been selected in such a way as to be consistent with the usual technical measurements of q (the rate of corrosion) in milligrammes decimetres^{-2} days^{-1} or $8 \cdot 64 \times 10^9$ C.G.S. units. E (the corrosion cell e.m.f.) in volts has been taken as defining the fourth fundamental unit in this system.   The complete set of corrosion properties will thus be measured in decimetres, milligrammes, days and volts or in d.m.d.v. units.

Two new quantities are introduced in this table, namely K and ξ, the former defined by

$$K = \frac{\partial C}{\partial E} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

and the latter by

$$\xi = \frac{\partial \rho}{\partial C} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

K is thus a measure of the capacity of the system for the corrodant, or the quantity in solution required to change the overall cell e.m.f. by one volt ;   and ξ, a dimensionless quantity, is defined as the change in density produced by unit change in the concentration of the corrodant.   The diffusivity term D_c is simply defined by analogy with the thermometric conductivity or thermal diffusivity.

EXPERIMENTAL MEASUREMENTS ON FORCED CONVECTION.

In these experiments the body of the metal corroded took the form of a cylindrical tube, being part of a pipe system through which the corrodant flowed at a measured rate.   The test piece fitted flush into glass pipes of the same diameter so that no eddies were created by any discontinuity in the rate or direction of flow.   The test piece was weighed before and after a measured time interval during which the flow rate (Γ) has been maintained constant.   From a series of such measurements on any one tube, q could be measured as a function of Γ.   Various tubes of copper, brass, phosphor bronze and mild steel of different lengths and diameters were used.   The resultant q versus Γ curves were all of the same form.   Very low rates of flow produced no increase in the rate of corrosion.   Further increase in the flow rate resulted in a sharp increase in the rate of corrosion, but at still higher flow rates the rate of corrosion again became independent of the rate of flow.   An increase in corrosion rate with flow rate has been recorded by Hatch and Rice (1945).   In all the examples studied the velocity of flow required to give practically a stationary final corrosion rate were well within the region of laminar flow.   Figure 1 gives some illustrative results obtained in the study of corrosion of a mild steel tube $10 \cdot 0$ cms. long and $0 \cdot 33$ cm. internal diameter, by a 60/40 acetic acid acetic anhydride mixture ;   and Figure 2 similar results from a copper tube $15 \cdot 6$ cms. long and $0 \cdot 454$ cm. internal diameter, both at 20° C.   The group of curves shown in Figure 3 refer to the corrosion of copper tubes of the various lengths and diameters indicated on the legend, exposed to a 50% aqueous acetic acid solution.   The tubes were prepared from a given batch of copper and were given an identical heat treatment and finally quenched in alcohol just before use.   The corrosion rates for very fast and very slow rates of flow were independent of the diameters of the tubes.   At intermediate rates the shorter and finer tubes corroded relatively faster than the longer and wider ones.

THE PROBLEM OF HEAT LOSS UNDER FORCED CONVECTION.

The problem of the change in heat transmittance (h) with change in the velocity of flow in a pipe has been subject to considerable study and experimental results have been co-ordinated by means of dimensionless quantities.
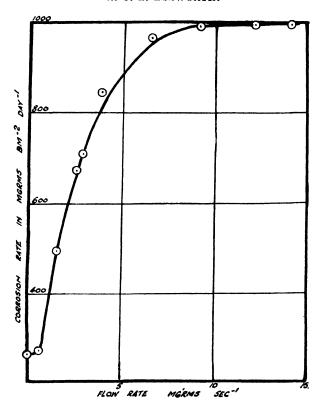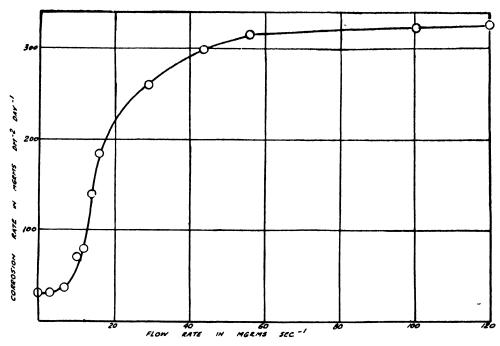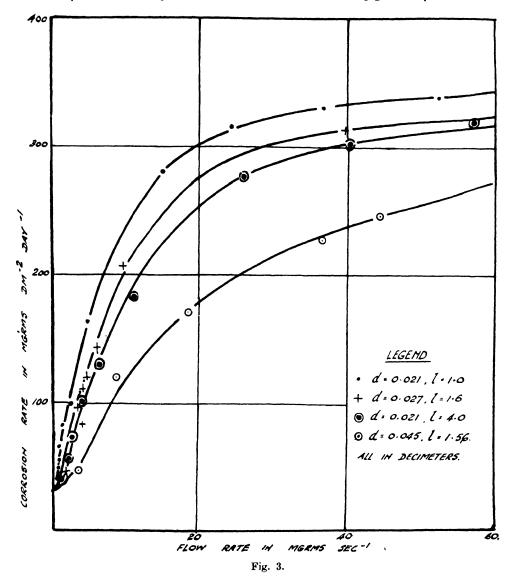
Fig. 1.

Fig. 2.

For heat transference in the region of laminar flow McAdams (1942) gives the expression

$$\frac{hd}{k_\theta} = 2 \cdot 01 \left(\frac{\Gamma c_p}{kl}\right)^{1/3} \left(\frac{\eta}{\eta_w}\right)^{0 \cdot 14}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where η is the viscosity of the fluid in the centre of the pipe and η_w that at the

Fig. 3.

walls. The other symbols have the meanings outlined in Table 1. When convection is transporting not heat but the soluble products of corrosion there is no reason why the viscosity at the walls should be significantly different from that at the centre of the pipe. Equation (3) transposed to quantities concerned with corrosion will therefore take the form

$$\frac{qd}{j(1 - q/q_0)} = 2 \cdot 01 \left(\frac{\Gamma K}{jl_\rho}\right)^{1/3} E^{1/3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where the symbols again have the meanings given in Table 1.   Equation (4) may be rewritten as

$$\frac{1}{q} - \frac{1}{q_0} = 0 \cdot 498 \left(\frac{d^3 l}{\overline{\Gamma}}\right)^{1/3} \left(\frac{\rho}{\overline{KE} j^2}\right)^{1/3}$$

or

$$\frac{\partial \left(\frac{1}{q}\right)}{\partial \left(\frac{d^3 l}{\Gamma}\right)^{1/3}} = 0 \cdot 498 \left(\frac{\rho}{\overline{KE} j^2}\right)^{1/3} \quad \dots\dots\dots\dots\dots\dots \quad (5)$$

LEGEND

○ MILD STEEL IN 60/40 ACID/ANHYD

◯ COPPER IN 60/40 ACID/ANHYD.

⊕ PHOSPHOR BRONZE IN 60/40 ACID/ANHYD

◯ COPPER IN 50% AQUEOUS ACETIC ACID
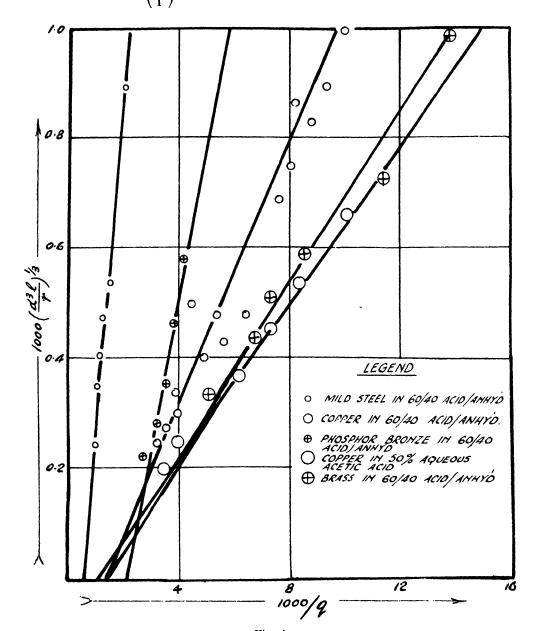
⊕ BRASS IN 60/40 ACID/ANHYD

Fig. 4.

So that experimental results may therefore be fitted to this equation by plotting $1/q$ versus $\left(\dfrac{d^3l}{\Gamma}\right)^{1/3}$. The results treated in this way are shown in Figure 4. The experimental points for each system studied lie on a straight line, giving a positive intercept on the $1/q$ axis. The slopes of these lines are a measure of the quantity $\left(\dfrac{\rho}{KEj^2}\right)$. Thus we have

$$\left(\frac{\rho}{KEj^2}\right)^{1/3} = 2\cdot 01\; \frac{\partial\left(\dfrac{1}{q}\right)}{\partial\left(\dfrac{d^3l}{\Gamma}\right)^{1/3}} \quad \dotfill \quad (5a)$$

$\qquad = 16\cdot 1$ d.m.d.v. units (copper in 60/40 acetic acid-acetic anhydride).

$\qquad = 29\cdot 1$ d.m.d.v. units (copper in 50% aqueous acetic).

$\qquad = 3\cdot 32$ d.m.d.v. units (mild steel in 60/40 acetic acid-anhydride).

$\qquad = 7\cdot 44$ d.m.d.v. units (phosphor bronze in 60/40 acetic acid-anhydride).

$\qquad = 26\cdot 1$ d.m.d.v. units (brass in 60/40 acetic acid-anhydride).

The values of the densities ρ in d.m.d.v. units are :

$\qquad 1\cdot 056\times 10^6$ for 50% aqueous acetic acid and

$\qquad 1\cdot 060\times 10^6$ for 60/40 acetic acid acetic anhydride.

Using the values of j from the earlier paper, we may now compute the values of the product KE for the five examples above. An independent measurement of E (from over-voltage measurements or from the Gibbs' free energy of the corrosion reaction) is necessary before we can derive the values of the capacity terms K. However, for many purposes the product KE is all that is required. Thus the coefficient of diffusion D_c of the depolarizing agent is related to j and KE by the expression

$$D_c = \frac{j}{KE} \text{ decimetres}^2 \text{ day}^{-1}$$

$$= 1\cdot 16\times 10^{-3} \; \frac{j}{KE} \text{ cms.}^2 \text{ sec.}^{-1}.$$

Values of KE and D_c computed from the figures above are given in Table 2.

TABLE 2.

Metal.	Corrodant.	KE in d.m.d.v. Units.	D_c in d.m.d.v. Units.	D_c in C.G.S. Units.
Copper	50% aqueous acetic.	1·20	5·0	0·0058
Copper	60/40 acetic acid-acetic anhydride.	2·3	4·6	0·0053
Mild steel ..	60/40 acetic acid-acetic anhydride.	10·8	4·8	0·0056
Brass	60/40 acetic acid-acetic anhydride.	1·5	4·1	0·0048
Phosphor bronze	60/40 acetic acid-acetic anhydride.	4·2	4·3	0·0050

R. C. L. BOSWORTH.

It will be observed from this table that whereas the values of KE vary practically over a tenfold range the values of the diffusivities are, within the limits of an experimental error accentuated by the act of cubing, constant. It therefore appears that these observations lend support to a suggestion that the same depolarizing agent is concerned in all these cases. The absolute magnitude of the diffusion coefficient is considerably higher than those usually given by liquid systems. Thus Sherwood (1937) claims that the diffusivities of most organic and inorganic matter in liquids lie between $0 \cdot 3$ and $1 \cdot 5 \times 10^{-5}$ cms.^{2} sec.$^{-1}$, or about 3×10^{-3} of the figures estimated above for the diffusivity of the depolarizing agent.

SUMMARY.

The rate of corrosion of metal tubes through which a corrodant liquid is caused to flow has been measured as a function of the rate of flow. The rate of corrosion increases as the flow rate increases but becomes practically stationary when the rate of flow is still quite low.

The variation of the rate of loss of matter with the rate of flow takes the same form as that for the rate of loss of heat from a geometrically similar lagged hot pipe through which a conducting fluid is caused to flow.

The diffusivity of the depolarizing agent, defined as an expression analogous to the thermometric conductivity, proves to be the same for all metals and corrodants studied, and is of the order 5×10^{-3} cms.^{2} sec.$^{-1}$.

A table is given showing the properties concerned in the convective loss of heat together with the corresponding terms involved in the convective transfer of matter concerned in the process of corrosion.

REFERENCES.

Agar, J. N., 1947. *Farad. Soc. Discussion*, 1, 26-37.

Bosworth, R. C. L., 1949. THIS JOURNAL, 83, 8.

Hatch, G. B., and Rice, O., 1945. *Ind. Eng. Chem.*, 37, 752-759.

Levich, B., 1942. *Acta Physiochem.*, 17, 257.

———— 1944. *Ibid.*, 19, 117.

———— 1947. *Farad. Soc. Discussion*, 1, 37-43.

McAdams, W. H., 1942. Heat Transmission, p. 190. McGraw Hill, New York.

Nernst, W., 1904. *Z. Physik. Chem.*, 47, 52.

Sherwood, T. K., 1937. Absorption and Extraction. McGraw Hill, New York.

THE INFLUENCE OF NATURAL CONVECTION ON THE PROCESS OF CORROSION.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

INTRODUCTION.

Two earlier papers (Bosworth, 1949a, 1949b) have traced a degree of parallelism between heat loss by conduction and convection and matter loss by corrosion under conditions of forced convection and in circumstances in which all convection currents have been eliminated by the use of guard rings. The present paper extends this study to the consideration of natural convective losses from cylindrical bodies placed horizontally in a corrodant liquid. The convective heat loss from cylindrical bodies such as hot wires or steam pipes immersed in fluids has, on account of its economic importance, been subject to very considerable detailed examination. A fairly complete review of the findings in this field have been given by Lander (1942). For convective heat loss from horizontal cylinders the emittance q is related to the other physical variables by means of the dimensionless equation

$$\frac{qd}{k\theta} = F\left(\frac{d^3\rho^2g}{\eta k}\ \frac{cp}{}\ \beta\ \theta\right) \quad \dots\dots\dots\dots\dots \quad (1)$$

where the symbols have the meanings given in Table 1 of the previous paper (Bosworth, 1949b) and $F(\ )$ is a function which has been determined experimentally.

The methods of correlating experimental data expressed by means of equation (1) have been extended by analogy with the problems of the convective loss of matter by evaporation. Thus Sutton (1934), Powell and Griffiths (1939) and Pasquill (1943) have shown that losses by evaporation follows laws analogous to the loss of heat from similarly shaped hot bodies. The convective loss by corrosion, in as much as the rate is controlled by the conveyance of the active constituent to the surface and the removal of the products of reaction by convective currents set up as a result of the density changes produced by the reaction, appears to be quite analogous to the convective loss of water by evaporation with the simple difference that the convective current now flows downwards past the corroding body. If we transpose equation (1) over to properties concerned with corrosion according to Table 1 of the previous paper (Bosworth, 1949b) we get

$$\frac{qd}{j(1-q/q_0)} = F\left(\frac{d^3g\xi K^2E^2}{\eta j(1-q/q_0)}\right) \quad \dots\dots\dots\dots\dots \quad (2)$$

EXPERIMENTAL.

The validity of equation (2) has been tested experimentally by placing a number of cylinders of different metals and different diameters in a horizontal position at a given depth (2 cms.) below the free surface of different corrodant liquids in such a way that the cylindrical and not the end faces could be attacked. After standing in a thermostat for a given time, ranging from 24 to 168 hours, the samples were removed and weighed and the corrosion rates (q) determined. The metals investigated included deoxidized copper, mild steel, phosphor bronze and a brass (37% Zn, 63% Cu).

Of the various factors which occur in equation (2), the values of j (the corrosion conductivity) and q_0 (the maximum corrosion rate) have been determined by experiments on the guard ring equipment (Bosworth, 1949a). The product KE has likewise been determined (for the systems studied) by measurements under conditions of forced convection (Bosworth, 1949b). Figures for η, the viscosity of the corrodant medium, are readily available, so that there remains only the quantity ξ to be determined before equation (2) may be put to an experimental test. This factor may be computed from observations of the density of the corrodant before and after a given quantity of each metal has been dissolved in a known volume. Samples of the corrodant were therefore collected after various measured masses of each metal had dissolved in a known volume and their densities were determined by pyknometer measurements in a constant temperature room.

<center>RESULTS.</center>

The results obtained from the study of corrosion from horizontal cylinders are summarized in Figure 1, in which the corrosion rates for various metals, in each of a number of selected corrodants at 20° and 70°, are plotted against the
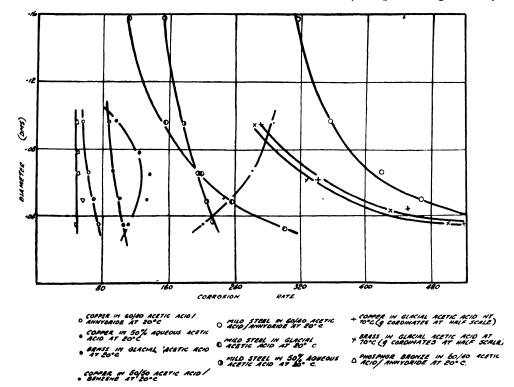

Fig. 1.

diameter of the specimen. In order to present as much data as possible on the one graph the scale for the q (or corrosion rate) axis referring to measurements at 70° C. is half that used for the measurements at 20° C.

It will be observed from the figure that for those systems in which the corrosive action is comparatively mild the rate of corrosion (in units of mass lost per unit area per unit time) varies only slightly with the diameter, and varies in such a way that the rate is somewhat faster for the smaller specimens. For

systems in which the corrosion rate is faster, such as mild steel at 20° C. or the copper alloys at 70° C., the variation of q with d (the diameter) is much more pronounced, so much so that for these systems the product qd (or the mass loss per unit length per unit time) is practically a constant. The one system examined with a very large value of j at room temperature (namely copper in 50% acetic acid 50% benzene) also gave a big variation of q with d, but one in the opposite direction, i.e. one in which the larger specimens corroded relatively faster than the smaller.
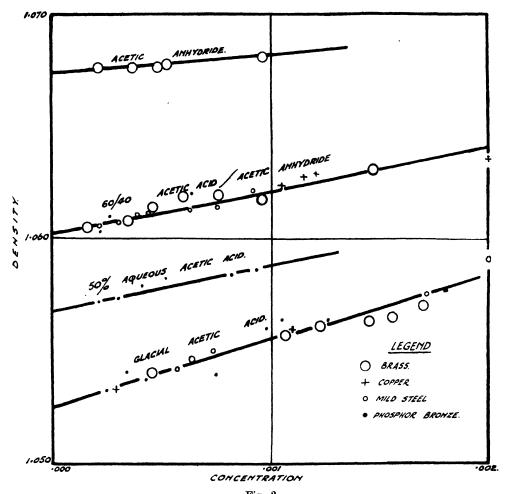
Fig. 2.

The dimensionless quantity ξ referred to above is defined as the ratio of the density change produced to the concentration of corroded metal measured in units of mass per unit volume of corrodant. While some water was formed during the corrosion action, represented chemically by

$$M + 2HAc + \tfrac{1}{2}O_2 = MAc_2 + H_2O,$$

where M represents any divalent metal; the corrodants examined were hydroscopic in nature and care was necessary in order to prevent the condensation of additional water from the atmosphere with consequent dilution of the corrodant. Figure 2 shows densities plotted against the concentrations for some of the

FF

systems studied. It will be seen that the different metals and alloys studied do not give significantly different results with respect to this property. The different fluids tested do however behave differently, the lower the density of the fluid the more pronounced the density change produced by dissolving a given small quantity of metal in it. The values of ξ from Figure 2, with the associated values of ρ, the original densities of the corrodants, are given in Table 1.

TABLE 1.

Corrodant.	Density ρ.	ξ.
Acetic anhydride	1·0674	0·7
60/40 acetic acid-acetic anhydride ..	1·0602	1·7
50% aqueous acetic acid	1·0568	2·0
Glacial acetic acid	1·0524	3·0
50/50 acetic acid-benzene	0·9475	12·0

CORRELATION OF RESULTS ON NATURAL CONVECTION.

We have now found, in the case of four of the systems studied, all the data necessary in order to compute the magnitude of both of the dimensionless quantities in equation (2). These systems are : copper in 50% aqueous acetic acid, and copper, mild steel, brass and bronze in the 60/40 acetic acid—acetic anhydride mixture. In Figure 3 the data for these systems, each represented by distinctive points, are shown plotted as

$$\log \frac{qd}{j(1-q/q_0)}$$

versus

$$\log \frac{d^3 g \xi K^2 E^2}{\eta j(1-q/q_0)}.$$
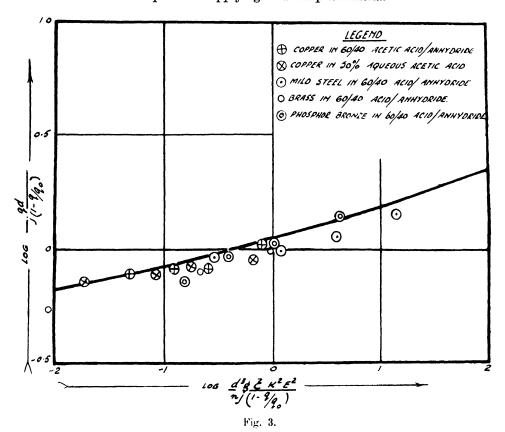
The full line shown on the figure is the curve for the corresponding dimensionless quantities involved in the loss of heat from horizontal cylinders by natural convection. This curve was taken from the paper by Lander (1942). The excellent agreement between the points, for the corrosive loss of matter by natural convection; and the curve, for the loss of heat from geometrically similar bodies by thermal convection, is a very clear indication that the phenomena involved are similar and the process which removes the products of corrosion from a surface and brings a continuous supply of the depolarizing agent is essentially the same as that involved in the removal of heat by the natural convection currents.

Data for correlation of all the curves shown on Figure 1 in terms of the dimensionless quantities shown in Figure 3 are not yet complete, mainly because sufficient independent values of KE are not available. However, if we assume that corrosion data would follow the heat convection curve over a wider range than shown above we may make certain interesting deductions the implications of which will be examined in a following paper. It has been shown that, for higher temperature corrosion, the product qd is practically a constant. In heat flow problems the corresponding quantity also becomes practically constant when the right-hand side of equation (1) is made less than about 10^{-4} (Bosworth, 1944). We conclude, then, that the condition $qd =$ a constant in a corrosion problem means that the right-hand side of equation (2) is very small. This might be effected, for example, by the value of K decreasing with increase in temperature, a fact which becomes significant when an attempt is made to interpret K in terms of the physical and chemical properties of the solution.

CONCLUSIONS.

As a result of the study of mild steel and copper alloys in acetic acid and acetic anhydride mixtures under such physical conditions that the removal of the products of reaction from the corroding surface takes place in a closely defined manner, it is concluded that an analogy may be set up between the rate of matter loss by corrosion on the one hand and the rate of heat loss from a lagged hot body on the other. Further, when the physical variables concerned with each phenomena are expressed as dimensionless products corresponding to the Nusselt number and the product of the Grashof and the Prandtl numbers respectively, the same function expresses the relationship between the parallel sets of dimensionless products applying to both phenomena.

Fig. 3.

This result suggests that a method for estimating the behaviour of large-scale metal members subject to corrosion could be established by setting up an appropriate thermal model. However, it must be emphasized that the principles as developed in these three papers apply at the moment only to a restricted field of corrosion problems—namely to those in which bimetallic corrosion cells are absent and in which the products of corrosion do not form insoluble films and thus give rise to a type of restriction to the flow of matter, of which a counterpart is not realized in the convective flow of heat.

SUMMARY.

The corrosive loss of matter from a metal cylinder immersed horizontally in a corrodant liquid at a constant temperature has been measured for a number

of specimens of different diameters. The metals investigated included mild steel, copper and various copper alloys; the liquids acetic acid and acetic anhydride mixtures. In most cases q (the corrosion rate) tends to increase as d (the diameter) is decreased and in some cases the product qd is practically constant.

When the dimensionless products of the properties involved in corrosion analogous to the Nusselt, Prandtl and Grashof numbers are set up, the functional relationship between them is shown to be the same as that applying to the convective loss of heat from geometrically similar bodies.

It is suggested, therefore, that under certain conditions the use of thermal models could be a useful tool in extrapolating corrosion data from small to large-scale equipment.

REFERENCES.

Bosworth, R. C. L., 1944.   THIS JOURNAL, **78**, 220-225.
————————————— 1949*a*.   THIS JOURNAL, **83**, 8.
————————————— 1949*b*.   THIS JOURNAL, **83**, 17.
Lander, C. H., 1942.   *Inst. Mech. Engrs. J. and Proc.*, **148**, 81-112.
Pasquill, F.. 1943.   *Proc. Roy. Soc.*, A **182**, 75-95.
Powell, R. W., and Griffiths, E., 1939.   *Trans. Inst. Chem. Engs.*, **36**, 125-143.
Sutton, W. G. L.. 1934.   *Proc. Roy. Soc.*, A **146**, 701-722.

THE FORMATION OF MOBILE AND IMMOBILE FILMS OF OXYGEN ON TUNGSTEN.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

INTRODUCTION.

The contact potential method of studying the properties of films on metal surfaces has been developed into a tool suitable for both electro-positive and electro-negative films (Bosworth and Rideal, 1937; Bosworth, 1945). Since the contact potential difference between a covered and a bare surface is an easily measurable index of the fraction (θ) of the surface covered, it can be used to record the changes in θ which follow such surface processes as evaporation and condensation. This paper will be devoted to an application of the contact potential method to the study of the condensation of oxygen on tungsten.

An analysis by Roberts (1935, 1938) of the kinetics of adsorption with dissociation of a diatomic gas has shown that condensation proceeds far more slowly if the film formed is mobile than if the film formed is immobile, particularly when the interaction between the adsorbed atoms (or adatoms) is large. For the rate of change of θ (with time) Roberts gave the expression

$$\frac{d\theta}{dt} = \frac{2}{n_s} \frac{\alpha_2 p_2}{\sqrt{2\pi mkT}} \varphi(\theta), \quad \dots\dots\dots\dots (1)$$

where n_s is the number of spaces per unit area available for adsorption.

α is the condensation coefficient.

p is the pressure due to the molecules.

m is the mass of a single (diatomic) molecule.

k is the Boltzmann gas constant,

T is the absolute temperature, and

$\varphi(\theta)$ is a function derived by Roberts.

For an immobile film the function $\varphi(\theta)$ takes the form

$$\varphi(\theta) = 1 - 1 \cdot 75(\theta - 0 \cdot 3215\theta^2 - 0 \cdot 0833\theta^3 - 0 \cdot 0175\theta^5) \quad \dots\dots (2)$$

For a mobile film $\varphi(\theta)$, while practically the same as for the immobile film at low values of θ, decreases much more rapidly as θ increases and, over the higher values of θ, assumes a value which depends on the interaction energy of the adatoms, being the smaller the higher this energy.

The fraction of the surface covered at which $\varphi(\theta)_{\text{mobile}}$ becomes significantly less than the corresponding value of $\varphi(\theta)_{\text{immobile}}$ depends on the lattice arrangement on the surface. If each adsorption space on the surface has four near neighbours the value of θ at which the difference becomes significant is a little less than $0 \cdot 5$. If the adsorption space has six near neighbours, this value of θ is just under $0 \cdot 33$.

Many of the adsorbed films for which the property of surface mobility has been studied have shown immobility at low temperatures and mobility at higher temperatures (Bosworth, 1942). Accordingly it was considered desirable to study the condensation of oxygen on tungsten over a range of temperatures. Any occurrence of appreciable surface migration in times of the order of the

interval between two successive collisions of a gaseous oxygen molecule at the same lattice point should mean a change in the kinetics of the condensation process at a temperature marking the inception of the surface migration.

EXPERIMENTAL.

The apparatus used consisted of a tube for the measurement of contact potential differences of the type already described (Bosworth and Rideal, 1937). A sketch of the apparatus used has been given by Bosworth (1945a). In addition to the normal two crossed tungsten filaments the tube contained a barium oxide coated nickel filament which had been previously heated in an oxygen atmosphere in order to convert the coating into BaO_2. When all the parts had been assembled the tube was exhausted, using a two-stage mercury diffusion pump; and all the metal parts, with the exception of the BaO_2 coated filament, were thoroughly outgassed. Sodium metal was then distilled into the vessel in order to produce a mirror on the glass walls, but not on the metal filaments, which were maintained hot during this process. The vessel was finally sealed off under vacuum.

Any desired oxygen pressure could now be maintained in the tube first by immersion in a liquid air bath and then by heating the BaO_2 coated filament with a known current. This produced an evolution of oxygen at a fixed rate; and since every oxygen molecule striking the cooled walls was immobilized by the sodium film, this also resulted in a fixed oxygen pressure which could be varied at will by varying the heating current to the oxygen-emitting filament.

The current-temperature curves for the two cross filaments were obtained by measuring the current-resistance characteristics at temperatures below 1000° K., and the current-brightness temperature curve (using an optical pyrometer) in the higher temperature range.

Contact potential differences were obtained by drawing the infrasaturation curve from emitter filament to collector filament. The former was maintained at a fixed temperature of the order 2500° K., while the latter was taken through a series of small external potential differences (from −2 volts to +1 volt) with respect to the central point of the hot filament. A string galvanometer with recording camera was used to follow rapid changes in the contact p.d. The method of working was as follows: A stable equilibrium film was allowed to build up on the collector filament and a series of snapshots of the galvanometer string taken with the camera, over a range of external applied potentials. A suitable external potential was then selected so that the expected curve for the variation of the emission with change in the contact potential difference consequent on a change in the chemical nature of the surface film should lie wholly within the range of the camera. The oxygen pressure was adjusted to the desired figure by means of the current through the barium dioxide source and the collector filament was heated to 2200° C. to clean it. The camera drive was then set going. The collector filament temperature was then dropped to the figure at which condensation was to be studied by suddenly changing the heating current. Initially rapid changes in galvanometer current occurred and the camera was stopped when this change became substantially constant. Further records were then obtained by reflashing the collector filament and then dropping the temperature to some other point in the condensing range (90 to 1000° K.). As explained above, changes in the oxygen pressure could be effected by changing the heating current on the BaO_2 source. The relative pressures attained could be measured from the slope of the initial part of the condensation curve or from the whole of the condensation curve at 90° K., at which temperature condensation follows entirely the mechanism associated with the immobile film.

EXPERIMENTAL RESULTS.

The results accruing from the various experimental runs were collected in the first instance in the form of records of the infrasaturation emission versus time curves for the various experimental conditions studied. Using the known current-volts characteristic of the assembly, the curves were first changed to contact p.d. versus time curves and then by means of the relationship between the contact p.d. and θ found earlier for oxygen on tungsten films (Bosworth, 1945b) were finally converted to θ versus time curves. Some illustrative curves of this nature are shown in Figures 1 and 2.

FIG. 1.
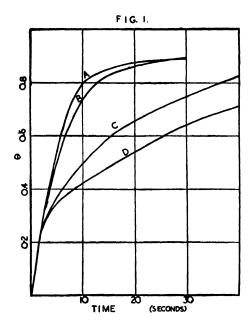
Figure 1 refers to condensation at a fixed oxygen pressure of $1 \cdot 1 \times 10^{-6}$ mms. of mercury and at a series of different temperatures. Curve A records the process of condensation at 90° K., curve B condensation at 540° K., curve C at 690° K., and curve D at 920° K.
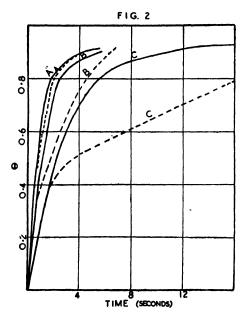
Figure 2 refers to condensation at a pair of fixed temperatures, one each in the mobile and the immobile range, and at a series of different oxygen pressures. Curves AA record condensation at a pressure of $7 \cdot 4 \times 10^{-6}$ mms. of mercury, curves BB at $4 \cdot 4 \times 10^{-6}$ mms., and curves CC at $2 \cdot 0 \times 10^{-6}$ mms. In each case the heavy lines refer to condensation at 90° K. and the broken lines to condensation at 830° K.

It will be observed that at about $\theta = 0 \cdot 5$ or a little less the condensation proceeds the more slowly the higher the temperature at any fixed pressure, and more than proportionally slowly the lower the pressure at any fixed temperature. These results are not such as would be expected from the simple Roberts' theory.

THEORY.

In the Roberts' theory for the condensation of a completely mobile film the condensation proceeds the more slowly the lower the quantity (η) or $e^{-V/kT}$, in which V is the interaction energy between a pair of atoms on the surface. V varies only slowly with the temperature. Accordingly η is expected to increase with an increase in temperature. Condensation on a completely mobile film is

thus expected to proceed more rapidly at higher temperatures and this, as pointed out above, is not observed. However, a sudden onset of a mobility on the surface akin to a type of two-dimensional melting is also a phenomenon which has only been recorded in a few special cases. Much more usually the process of acquiring a state of surface mobility is more akin to a two-dimensional vaporization. On the picture given by Lennard Jones (1937) the mobile adatom is in a certain state of high energy and remains in that state for a finite time before being deactivated to return to the normal state of being fixed to a given lattice point. In this static condition the adatom remains, on the average, for a much longer time interval before being reactivated to the mobile condition. At any given instant the number of adatoms in the mobile state is only a small fraction of the total number. In considering the effect of activated mobility on the rate of condensation it would appear that the important factor is the probability of a given adsorbed atom migrating to a neighbouring lattice point before that point suffers a collision from a component atom of a gaseous molecule. Higher surface temperatures are associated with more frequent activations to the mobile state and therefore at such temperatures the film behaves as though it

FIG. 2

were more completely mobile in the Roberts sense. Again at lower pressures the time intervals between successive collisions become longer, so that the film also behaves as though it were more mobile.

At any fixed temperature and pressure the rate of condensation of a (truly) mobile film depends on the quantity η.

$$\eta = e^{-V/kT},$$

where V is the interaction energy between a pair of adatoms. Above a value of θ of about $0 \cdot 5$ the rate of condensation becomes practically zero when η is small. For oxygen on tungsten films we may estimate V from the figures given by Bosworth (1945) for the heat of evaporation of oxygen from nearly bare and from completely covered surfaces. These heats are respectively 154,000 and 66,000 calories per gramme molecule. Since each lattice point on the 110 surface plane has six almost equidistant neighbours, and further since dipole interaction as calculated by the Topping equation is negligible in comparison

with the total interaction, we may neglect all interaction other than that between near neighbours and write

$$V = \frac{154,000 - 66,000}{6}$$

$$= 14,700 \text{ calories per gramme molecule.}$$

For a temperature of 750° K., therefore,

$$\eta \text{ becomes } 0 \cdot 000068,$$

at which figure the value of $\varphi(\theta)_{\text{mobile}}$ becomes very small in comparison with $\varphi(\theta)_{\text{immobile}}$.

We are now in a position to attempt a computation, from the observed rates of condensation, of a number of adatoms which become mobile in a given time. Let $\left(\dfrac{d\theta}{dt}\right)_{\text{im.}}$ represent the rate of growth of the film calculated from the theory of immobile condensations for given conditions of θ, temperature and external pressure and let $\left(\dfrac{d\theta}{dt}\right)_{\text{obs.}}$ be the actual observed rate of growth under the given conditions. In addition to the variables which enter into the determination of $\left(\dfrac{d\theta}{dt}\right)_{\text{im.}}$ the observed rate of condensation also depends on the state of distribution of the adatoms on the surface at the moment when further condensation takes place. This distribution of the adatoms on the surface may be characterized by two limiting states; a state α in which every atom is attached at the point at which it made the initial collision with the surface and a state β in which surface spreading forces have attained equilibrium with thermal agitation. Condensation on a surface in state α will proceed at the rate $\left(\dfrac{d\theta}{dt}\right)_{\text{im.}}$. Condensation on a surface in state β (provided $\theta > 0 \cdot 5$) will proceed at a rate which may be taken as negligibly small in comparison with $\left(\dfrac{d\theta}{dt}\right)_{\text{im.}}$. Surface migration results in a change from the state α to the state β, and will be assumed to follow a " unimolecular " law, viz.

$$\frac{da}{dt} = -\varkappa a$$

or

$$a = 1 - e^{\varkappa t_1}$$

where a represents the fraction of the covered surface in the state α, and t_1 is effectively the time elapsing between two successive collisions at two neighbouring lattice points on the surface. This time depends on the rate at which gaseous molecules impinge effectively on the surface. For immobile condensation the data of Roberts shows that the integral
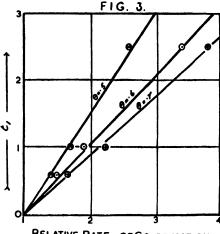
$$\int_0^\theta \frac{d\theta}{\varphi(\theta)}$$

attains the value of $1 \cdot 0$ at $\theta = 0 \cdot 52$. Accordingly we take for t_1 the time taken for the film to build up from zero concentration to $\theta = 0 \cdot 52$ under the given external conditions and with the film immobile, i.e. condensation at low temperature.

We may now write for the rate of condensation

$$\left(\frac{d\theta}{dt}\right)_{obs.} = a\left(\frac{d\theta}{dt}\right)_{1m.}$$

$$= (1 - e^{-\varkappa t_1})\left(\frac{d\theta}{dt}\right)_{1m.}$$

$$\simeq \varkappa t_1\left(\frac{d\theta}{dt}\right)_{1m.},$$

so long as $\left(\frac{d\theta}{dt}\right)_{obs.}$ is not of a different order of magnitude to $\left(\frac{d\theta}{dt}\right)_{1m.}$.   Thus

FIG. 3.

RELATIVE RATE OF CONDENSATION

we have for the relative rates of condensation

$$\left(\frac{d\theta}{dt}\right)_{obs.} \bigg/ \left(\frac{d\theta}{dt}\right)_{1m.} = \varkappa t_1.$$

The value of t_1 may be read off from the curves shown on Figure 2 for the three different pressures employed. A plot of $\left(\frac{d\theta}{dt}\right)_{obs.} \bigg/ \left(\frac{d\theta}{dt}\right)_{1m.}$ versus t_1 is given in Figure 3 for the three different values of θ, viz. $0 \cdot 5$, $0 \cdot 6$ and $0 \cdot 7$ at 830° K. These points fall on satisfactory straight lines passing through the origin. From the slopes the values of $\varkappa$ may be read off. The values thus obtained are :

     At $\theta = 0 \cdot 5$, $T = 830°$ K., $\varkappa = 0 \cdot 66$ reciprocal seconds.
     At $\theta = 0 \cdot 6$, $T = 830°$ K., $\varkappa = 0 \cdot 95$ reciprocal seconds.
     At $\theta = 0 \cdot 7$, $T = 830°$ K., $\varkappa = 1 \cdot 28$ reciprocal seconds.

CALCULATION OF THE DIFFUSION COEFFICIENTS.

The values of $\varkappa$ deduced above may be taken as measures of the times elapsing between successive activations of the same adatom to the mobile state, and thus may be related to the coefficients of surface diffusion (D) by the expression

$$D = \tfrac{1}{2}\varkappa\lambda^2,$$

where λ is the mean free path of the diffusing adatom and may be taken as the distance between two neighbouring points on the surface lattice. With the

high interaction energy characteristic of the oxygen on tungsten films it is unlikely that a mobile adatom will move over several lattice points before deactivation. Once it has moved out of the range of immediate neighbours of any other adatom it is practically in a uniform field. Thus we have for the diffusion coefficient of oxygen on tungsten

$$D = 3 \cdot 7 \times 10^{-16} \varkappa \ \text{cms.}^2 \ \text{sec.}^{-1}.$$

At 830° K. the values of D are thus :

For $\theta = 0 \cdot 5$, $D = 2 \cdot 45 \times 10^{-16}$ cms.^{2} sec.$^{-1}$.
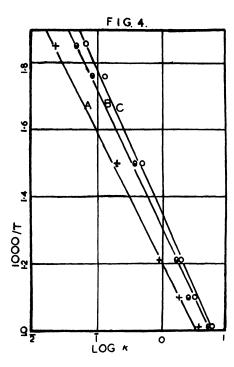
For $\theta = 0 \cdot 6$, $D = 3 \cdot 5 \ \times 10^{-16}$ cms.^{2} sec.$^{-1}$, and

For $\theta = 0 \cdot 7$, $D = 4 \cdot 8 \ \times 10^{-16}$ cms.^{2} sec.$^{-1}$.

From other measurements of $\varkappa$ it is possible to calculate D over a range of temperatures and values of θ. For an activated process we expect D to vary with temperature according to a relation

$$D = D_0 e^{-b/T}$$

where D_0 is a constant and b is a measure of the activation energy concerned. Some curves showing $\log \varkappa$ plotted against $1000/T$ are given in Figure 4. Curve A

F I G. 4.

refers to $\theta = 0 \cdot 4$, curve B to $\theta = 0 \cdot 5$, and curve C to $\theta = 0 \cdot 6$. Values of the activation energy computed from the slopes of these curves are :

For $\theta = 0 \cdot 4$, activation energy $0 \cdot 52$ electron volts.

For $\theta = 0 \cdot 5$, activation energy $0 \cdot 50$ electron volts.

For $\theta = 0 \cdot 6$, activation energy $0 \cdot 47$ electron volts.

For $\theta = 0 \cdot 8$, activation energy $0 \cdot 46$ electron volts.
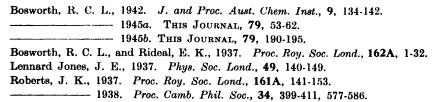
These figures for the activation energy for surface migration are only a small fraction of the corresponding figures for the heats of vaporization for these same films.

SUMMARY.

The contact potential difference has been used to study the condensation of oxygen on tungsten. At low temperatures the process follows the kinetics expected by the Roberts' theory of condensation with dissociation as an immobile film. At higher temperatures the condensation (once θ has exceeded a value of about $0 \cdot 4$) proceeds the more slowly the higher the temperature or the lower the pressure. This is interpreted as due to the activation of some of the adsorbed oxygen atoms to a mobile state which proceeds the more rapidly the higher the temperature and the more completely the lower the pressure.

Calculation of the surface diffusion coefficient at $830°$ K. gives a figure of $2 \cdot 5 \times 10^{-16}$ cms.^{2} sec.$^{-1}$ at $\theta = 0 \cdot 5$, increasing with increase in θ and an activation energy of $0 \cdot 50$ electron volts for $\theta = 0 \cdot 5$, this time decreasing with increase in θ.

REFERENCES.

Bosworth, R. C. L., 1942. *J. and Proc. Aust. Chem. Inst.*, **9**, 134-142.
———————————— 1945a. THIS JOURNAL, **79**, 53-62.
———————————— 1945b. THIS JOURNAL, **79**, 190-195.
Bosworth, R. C. L., and Rideal, E. K., 1937. *Proc. Roy. Soc. Lond.*, **162A**, 1-32.
Lennard Jones, J. E., 1937. *Phys. Soc. Lond.*, **49**, 140-149.
Roberts, J. K., 1937. *Proc. Roy. Soc. Lond.*, **161A**, 141-153.
——————— 1938. *Proc. Camb. Phil. Soc.*, **34**, 399-411, 577-586.

A NOTE ON THE SIGMA PHENOMENON.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

I. INTRODUCTION.

The sigma phenomenon, which has been described in some detail by Scott Blair (1938, 1944), is apparently of wide occurrence in the flow of semi-fluid pastes and slurries. In the method of studying the flow of such systems introduced by Schofield and Scott Blair (1930, 1931, 1935) we plot the mean velocity of the flow (U) against the stress (τ) at the wall. If the one system is studied in a series of pipes of different diameters we get a series of straight lines, one for each tube diameter. Let us call the slope of these lines ($dU/d\tau$) a quantity σ, and then proceed to plot σ against R, the radius of the tube. Were the fluid system studied to be Newtonian in behaviour, it would follow that the resultant plot would be a straight line passing through the origin and having a slope ($d\sigma/dR$) equal to $1/4\,\eta$, with η the viscosity. For systems exhibiting the sigma phenomenon the σ versus R plots are reasonable straight lines, but they do not pass through the origin, but instead give a positive slope σ_0 on the σ axis. Thus for such systems we have

$$\frac{dU}{d\tau} = \sigma_0 + \frac{R}{4\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In a paper by the author (Bosworth, 1947) it was shown that this equation had a form resembling that for the flow of a gas in a capillary at such a low pressure that slip flow was occurring, and it was further suggested that similar mechanisms for the transport of momentum from the fluid to the walls was operative. The peculiar properties of gas flow at low pressure are attributable to the fact that the carriers of momentum (viz. the moving molecules) travel through the system with mean free paths which are of the same order of size as the diameter of the tubes concerned. In seeking a similar mechanism for the transport of momentum in a semi-liquid slurry at atmospheric pressure it was suggested that the class of hypersonic longitudinal waves in the oscillatory motion into which the Debye theory of specific heats breaks up the thermal motion of condensed matter might contribute the momentum carriers with the long mean free paths. It will be the object of this paper to make an estimate of the magnitude of the sigma phenomenon in terms of the Debye distribution of frequencies. A similar estimate by the author (Bosworth, 1948) of the magnitude of the viscosity of normal liquids interpreted as a momentum transfer by transverse waves with mean free paths equal to the mean distance between two " holes " in the liquid has met with moderate success and will be used as a basis for the present calculation.

II. DERIVATION OF THE INTENSITY OF THE MOMENTUM FLOW.

Following the practice adopted in the earlier papers we will refer to the stream of acoustical radiation as a stream of " phonons " carrying quanta of energy and momentum given by the quantum rule. The energy per unit volume

dE associated with longitudinal waves of frequency lying between ν and $\nu + d\nu$ is given by

$$dE = \frac{4\pi h}{c_1{}^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

where c_1 is the velocity of propagation of the longitudinal waves. The number of phonons dn_p per unit volume derived from longitudinal waves in the frequency range ν to $\nu + d\nu$ (or phonons of class B) is expressed by the relationship

$$dn_p = \frac{4\pi}{c_1{}^3} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

The density of these same phonons $(d\rho_p)$ is likewise given by

$$d\rho_p = \frac{4\pi h}{c_1{}^5} \cdot \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (4)$$

While the number of phonons of class B striking unit area of the wall in unit time is

$$\tfrac{1}{4} \, dn_p \, c_1, \text{ or}$$

$$\frac{\pi}{c_1{}^2} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1}$$

A like number of phonons will leave the unit area of the wall in unit time in directions which are distributed according to the cosine law. A certain fraction
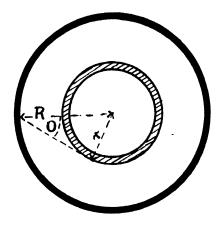
Fig. 1.

of that number will cross the surface of an inner cylinder of radius r. If R is the inner radius of the pipe (Figure 1) then phonons from any given point on the wall will cross the inner cylinder so long as they make an angle θ with the normal which is less than arc sin r/R, in a plane normal to the direction of flow.

The fraction crossing the inner cylinder is thus

$$\int_0^{\text{arc sin } r/R} \cos\theta \, d\theta = r/R.$$

If α is the absorption coefficient the number of phonons in unit time and from unit wall area which are absorbed between the radii r and $r - dr$ (the shaded area in Figure 1) is then

$$\frac{\pi}{c_1{}^2} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} \cdot \frac{r}{R} \cdot e^{-\alpha(R-r)} \alpha dr.$$

Let now u be the local velocity of flow of the zone of fluid represented by the shaded area. Generally u is a function of r. The momentum flow from unit area of the wall to an area r/R of the shaded zone and due to the phonons of class B now becomes

$$\frac{\pi}{c_1^4} \frac{u h \nu^3 d\nu}{e^{h\nu/kT}-1} \frac{r}{R} e^{-\alpha(R-r)}\alpha dr.$$

The total momentum flow to the shaded area carried by all the phonons arising from longitudinal waves thus becomes

$$\frac{\pi u r e^{-\alpha(R-r)}\alpha dr}{R c_1^4} \int_0^{\nu_0} \frac{h\nu^3 d\nu}{e^{h\nu/kT}-1} \quad \cdots\cdots\cdots\cdots \quad (5)$$

where ν_0 is the limiting Debye frequency. For all temperatures considerably in excess of the Debye characteristic temperature $\frac{h\nu_0}{k}$ we may write approximately

$$e^{h\nu/kT}-1 = h\nu/kT,$$

so that expression (5) becomes

$$\frac{\pi r e^{-\alpha(R-r)}u kT\alpha dr}{R c_1^4} \frac{\nu_0^3}{3} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (6)$$

But now ν_0 is related to the number N of molecules in unit volume by

$$\nu_0^3 = \frac{9N}{4\pi} \frac{1}{\left(\dfrac{1}{c_1^3} \quad \dfrac{2}{c_t^3}\right)}, \quad \cdots\cdots\cdots\cdots\cdots \quad (7)$$

where c_t is the velocity of propagation of the transverse hypersonic waves. As in the earlier paper, we assume that the Cauchy-Poisson relation holds between c_1 and c_t, namely that

$$5c_t^2 = 3c_1^2 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (8)$$

which on substitution in equation (7) gives

$$\nu_0^3 = 0\cdot1886 \frac{9}{4\pi} N c_1^3 \quad \cdots\cdots\cdots\cdots \quad (9)$$

and this, on substitution in expression (6), gives for the momentum transferred per unit time to the shaded area

$$0\cdot1414\ u e^{-\alpha(R-r)}\alpha dr\ \frac{r}{R} \frac{NkT}{c_1}.$$

This momentum flow yields a contribution $(d\tau)$ to the stress exerted by the fluid on the walls, namely

$$d\tau = 0\cdot1414\ \frac{uNkT}{c_1}\ \alpha e^{-\alpha(R-r)}dr \quad \cdots\cdots\cdots\cdots \quad (10)$$

The total stress on the walls due to the longitudinal waves becomes

$$\tau = 0\cdot1414\ \frac{\alpha kTN}{c_1}\ \int_0^R u e^{-\alpha(R-r)}dr \quad \cdots\cdots\cdots\cdots \quad (11)$$

Whenever sigma phenomena are in evidence there occurs considerable slip at the walls, thus u varies relatively slowly throughout the pipe except in the immediate vicinity of the walls. Under such conditions we may, without sensible error, take u outside the integral sign in equation (11) and replace it by U, the average velocity of flow in the pipe. Then we get

$$\tau = 0\cdot1414\ \frac{\alpha UNkT}{c_1}\ \int_0^R e^{-\alpha(R-r)}dr$$

$$=0\cdot 1414 \;\frac{UNkT}{c_1}\; e^{-\alpha R} \;\dots\dots\dots\dots\dots\dots (12)$$

as our final expression for the contribution to the stress on the wall due to the collision of photons originating from longitudinal waves.

III. THE MAGNITUDE OF σ_0.

On differentiation of equation (12) we obtain

$$\frac{dU}{d\tau}=\frac{7\cdot 07 c_1}{NkT}\; e^{\alpha R} \;\dots\dots\dots\dots\dots\dots (13)$$

Now from equation (1) we have for σ_0

$$\sigma_0=\frac{\lim}{R\to 0}\;\frac{dU}{d\tau}$$

$$=\frac{7\cdot 07 c_1}{NkT}$$

But since N is N/V where N is the Avogadro number and V is the molecular volume, and further since Nk is R, the ordinary gas constant, we get finally

$$\sigma_0=7\cdot 07\;\frac{Vc_1}{RT} \;\dots\dots\dots\dots\dots\dots (15)$$

For aqueous solutions c_1 is of the order $1\cdot 5\times 10^5$ cms. sec.$^{-1}$ and at room temperature RT is $2\cdot 5\times 10^{10}$ ergs. Accordingly, for such solutions we have for σ_0 the approximate value

$$\sigma_0=4\cdot 24\times 10^{-5}\; V \text{ cms.}^3 \text{ secs.}^{-1} \text{ dynes}^{-1} \dots\dots\dots\dots (16)$$

This estimated value of σ_0 may be compared with the experimental values of Schofield and Scott Blair (1930) for various aqueous pastes. Such a comparison would enable V, the effective molecular volume of the pastes, to be computed. In the table below the experimental values of σ_0 and the estimated values of V obtained therefrom are given in tabular form.

TABLE 1.
Effective Molecular Volumes Estimated from the Sigma Phenomenon.
(Data of Schofield and Scott Blair.)

Paste.	Percentage Solids.	σ_0 (cms.^{3} sec.$^{-1}$ dynes^{-1}).	V (Litres).
Clay	2·36	0·33	7·7
Kaolin	37·2	0·11	2·6
Plaster of Paris.. ..	5·8	0·017	0·40
Barytes	43·5	0·015	0·35
Subsoil	33·5	0·0055	0·13

These molecular volumes are very large and are more nearly appropriate to a gaseous rather than a liquid system. To the effusive transport of momentum resulting in the sigma phenomenon these slurries thus act as solutions which are very dilute on the molar basis.

SUMMARY.
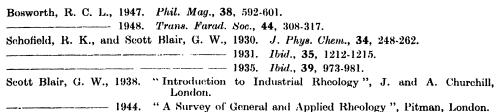
The suggestion that the sigma phenomenon observed in the flow of certain slurries is due to the transport of momentum to the walls by the acoustical vibrations into which the Debye theory resolves the thermal energy of the molecules is examined quantitatively. It is shown, subject to the assumptions

that the system is far above its Debye temperature and that the ratio of the velocities of the longitudinal and the transverse waves takes the Cauchy-Poisson value, that the value of σ_0 is given by

$$\sigma_0 = 7 \cdot 07 \ Vc_1/\mathbf{R}T,$$

where c_1 is the velocity of the longitudinal hypersonic waves and V is the effective molar volume of the slurry. Comparison of this equation with the measurements of Schofield and Scott Blair shows that V has a value of the order of a litre.

REFERENCES.

Bosworth, R. C. L., 1947. *Phil. Mag.*, **38**, 592-601.
——————————— 1948. *Trans. Farad. Soc.*, **44**, 308-317.
Schofield, R. K., and Scott Blair, G. W., 1930. *J. Phys. Chem.*, **34**, 248-262.
——————————————————————— 1931. *Ibid.*, **35**, 1212-1215.
——————————————————————— 1935. *Ibid.*, **39**, 973-981.
Scott Blair, G. W., 1938. " Introduction to Industrial Rheology ", J. and A. Churchill, London.
——————————— 1944. " A Survey of General and Applied Rheology ", Pitman, London.

A NOTE ON THE ESSENTIAL OIL OF *BACKHOUSIA ANISATA* VICKERY AND THE OCCURRENCE OF ANETHOLE.

By H. H. G. McKERN, A.A.C.I.

Although specimens from the myrtaceous tree *Backhousia anisata* Vickery, indigenous to the north coast of New South Wales, were collected as long ago as 1910, it has been confused with *Eugenia ventenatii*, and its taxonomic position was not established until recently by Vickery (1941).

On account of the strong aniseed-like odour of the crushed foliage it has received the vernacular name of " Aniseed Tree ", and this observation has prompted officers of the Forestry Commission of New South Wales to enquire into the economic value of the oil as a possible substitute for anise oil. This Institution has undertaken the examination of the oil obtainable from this species, and since a preliminary investigation shows promise of commercial value it has been decided to publish the results hitherto obtained. When further supplies of material become available, a more detailed examination of the oil will be made.

The examination so far shows that the foliage of this tree yields on steam-distillation 0·5% of a pale yellow oil strongly resembling anise oil of commerce in respect both to odour and taste. The principal component of the oil is anethole (*p*-propenyl anisole), present to the extent of about 60%, as compared with about 80% for anise oil. However, it is considered that by rectification or by freezing, a commercial equivalent of anise oil could be prepared, and would provide a local source of anethole. The oil of *B. anisata* is considered by the author to be far superior to fennel oil.

EXPERIMENTAL.

Samples of foliage were supplied by the Forestry Commission of N.S.W. Two collections were made, one, received 4/7/46, from one restricted locality in the Bellenger River area of New South Wales ; the other, received 11/11/46, was made up of foliage from three different and separated localities in the same area—Buffer Creek, Pine Creek and Kalang—the purpose of the second sample being to determine if the oil of this species is reasonably constant in composition to justify commercial exploitation.

Both samples consisted of leaves and terminal branchlets cut as for commercial distillation, and on steam-distillation they both yielded 0·5% of a pale yellow mobile oil, lighter than water and having a sweet taste and pronounced anethole-like odour. The oil froze readily to a crystalline mass on cooling in ice-water. The oils had the characteristics shown in the following table ; figures for the British Pharmacopœia specification for anise oil being given for comparison.

Preparation and Characterization of the Anethole.

Essential oil of *B. anisata* (47 g.) was frozen by cooling to about +5°. The crystalline mass was transferred to a chilled porous tile and pressed. By repetition of this process, 24 g. of white

	4/7/46 Sample.	11/11/46 Sample.	1932 B.P. Specifications. (Anise Oil).
Specific gravity at 20°/15·5°	0·9826	0·9806	0·980 to 0·994
Refractive index, at 20°	1·5535	1·5489	1·553 to 1·560
Optical rotation, 100 mm. tube	−1·15°	−1·88°	−2° to +1°
Freezing point	14·5°	12·0°	Not below 15°
Melting point	15·2°	13·2°	Not below 17°
Solubility in 90% V/V alcohol	Soluble in 1 vol.	Soluble in 1 vol.	Not more than 3 vols.
Ester number, mg. KOH per gramme	—	15·4	—
Ester number, mg. KOH/g, after acetylation	—	87·6	—

crystals were obtained, melting at 21°–22° to a colourless oil of powerful anethole odour and taste, and having the following characters :

$$d^{15}_{15} \qquad \qquad \qquad \qquad 0\cdot9912$$
$$n^{20}_{D} \qquad \qquad \qquad \qquad 1\cdot5613$$
$$\alpha_{D} \qquad \qquad \qquad \qquad \text{inactive.}$$

On oxidation of a portion with potassium permanganate by the procedure of King and Murch (1925), an excellent yield of a *solid acid* (neutral equivalent, 152) crystallizing in needles from hot water, and melting at 183–184° (uncorr.), was obtained. The melting point was not depressed by mixing with an authentic specimen of *anisic acid* (neutral equivalent, 152 (calculated)).

A further portion of the material was oxidized by the method of Shoesmith (1923) and a pale yellow liquid of aubépin odour resulted. It yielded a *p-nitrophenylhydrazone* m.p. 161·5° (uncorr.) undepressed by admixture with *p-anisaldehyde p-nitrophenylhydrazone*.

It is therefore concluded that the compound is *anethole*.

ACKNOWLEDGEMENTS.

REFERENCES.

King and Murch, 1925. *J. Chem. Soc.*, 127, 2640.
Shoesmith, J. B., 1923. *Ibid.*, 125, 2702.
Vickery, Joyce W., 1941. *Contrib. N.S.W. Nat. Herb.*, 1, 129.

The Museum of Technology and
    Applied Science,
    Sydney.

NITROGEN IN OIL SHALE AND SHALE OIL.

VIII. THE DETECTION OF TAR BASES.

GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

INTRODUCTION.

In connection with other aspects of this work it became necessary to develop an unambiguous test for the detection of tar bases in crude shale oil and its products.

The tar bases present in shale oil are principally pyridine homologues, though weakly basic pyrrole homologues are also present (Mapstone, 1948). Crude shale oil also contains a large proportion of non-basic nitrogenous compounds of unknown composition (Mapstone, 1949), but these were not of importance in the work described here. Tests carried out on the oil could indicate the presence of either pyridine homologues or of pyrroles, while tests on an acid extract of the oil would be mainly indicative of the pyridine bases because of the very low acid solubility of the pyrroles.

With strongly coloured samples, it was necessary to extract the bases with acid before applying the tests. A number of different tests were therefore examined for sensitivity for the detection of tar bases in solution in the lighter oils and in solution in dilute sulphuric acid as they were extracted from the darker coloured oils.

SAMPLES TESTED.

The tar bases present in the acid sludge from the treatment of cracked shale gasoline were considered to be sufficiently representative of those initially present in the gasoline to be used for this work. They were therefore isolated as described previously (Mapstone, 1947) and purified by distillation. They contained 8·69% of nitrogen by weight, and the bases present would be almost entirely pyridine homologues.

Since preliminary work indicated the probable presence of approximately 5 p.p.m. of tar bases in refined shale gasoline, another suitable tar base-free hydrocarbon solvent was required for the determination of the sensitivity of the various reagents. The highly purified n-heptane-isooctane blend used for the determination of the octane rating of motor fuels was found to give a negative test with all except a few of the reagents used. In the cases where a positive result was obtained the reaction could be attributed to other factors. A 1% solution of the bases in the heptane-octane mixture (hereafter referred to as gasoline) was carefully prepared and the more dilute solutions prepared from it by dilution with further gasoline.

A solution of the purified bases in dilute sulphuric acid was prepared by dissolving 1·0 ml. of the bases in 250 ml. of 0·097 N sulphuric acid. Titration of portion of the solution showed that the excess acid was 0·0637 N, giving an 0·0333 N solution of the bases. This solution was diluted with further portions of the 0·0970 N acid to give the more dilute solutions required.

The light recycle oil (boiling range 5% at 360° F., 95% at 520° F) from the thermal cracking of crude shale oil is dark brown in colour, and it was therefore

necessary to extract the bases for detection.   From the method of extraction
and the boiling range the bases would be principally pyridine homologues
together with any quinoline homologues that may be present.   Fifty millilitres
of the oil were washed with 200 ml. of 0·1061 N sulphuric acid.   Titration of
portion of the solution thus obtained showed that the excess acid was 0·0362 N,
giving an 0·0699 N solution of the bases.   This was diluted with further portion
of the 0·1 N acid to give the more dilute solutions required.

With crude shale oil it was even more necessary than with the light recycle
oil to extract the bases before detection.   In the manner described for the light
oil a 0·042 N solution of the bases from the crude shale oil was obtained in
0·1 N sulphuric acid.

Unless otherwise mentioned the tests on the hydrocarbon samples were
carried out by adding two drops of the reagent to 5 ml. of the sample, and the
tests on the acid extracts by adding four drops of the reagent to 1 ml. of the
sample.

REAGENTS.

In deciding which reagents were to be tested, those which reacted with
pyridine or quinoline or their homologues to give precipitates or developed
colours were chosen.   Since many alkaloids contain pyridine nuclei several
" alkaloid " reagents were included.   However, those alkaloid reagents which
are based on concentrated sulphuric acid (e.g. Froehde's, Mandelin's and
Erdmann's reagents) were not examined because of the action of the acid on the
olefines in the gasoline samples, and with the samples dissolved in dilute acid, the
dilution of the reagent would render them ineffective.

From the nature of their reaction with the tar bases the reagents were
somewhat arbitrarily subdivided into seven classes which are discussed in
turn.

(1) *Metal salts which precipitate the metal hydroxide.*

Pyridine and quinoline and their homologues are tertiary amines and their
aqueous solutions can be sufficiently alkaline to precipitate the hydroxides from
the solutions of the salts of various metals (Perkin, 1935).   The sensitivity of
the tests with such reagents would therefore depend principally on the solubility
of the hydroxide of the metal, and the ease with which it could be seen when
precipitated.   The reagents were prepared by adding dilute ammonia dropwise
to the aqueous solution of the metal salt until a slight permanent precipitate
was formed.   The reagent solution was used after filtration.

Five per cent. solutions of ferric chloride, cobalt nitrate, nickel nitrate,
cupric nitrate and zinc chloride and a saturated solution of potassium alum were
prepared in this manner.   Another mixed reagent was prepared by the addition
of 3 ml. of 1% ammonium aurine tricarboxylate solution to approximately
80 ml. of the saturated alum solution.   A slight red precipitate was formed and
removed by filtration.   It was thought that the dye would be adsorbed on any
aluminium hydroxide precipitate and render it more visible and thus possibly
increase the sensitivity of the alum reagent.

On carrying out the test on samples with higher tar base concentrations a
precipitate was thrown down but, with the limiting concentrations a film was
formed at the gasoline-reagent interface.   If an excess of reagent was used
(e.g. 2 ml. per 5 ml. sample) the cobalt and aluminium reagents gave positive
results even in the absence of tar bases.   It was therefore necessary to adhere
strictly to the test conditions in order to obtain reproducible results.   The
sensitivities of these reagents are presented in Table 1.   .

TABLE 1.

Sensitivities of Reagents.

Metal Salts which Precipitate the Metal Hydroxides.

Reagent.	Colour of Precipitate.	Sensitivity.[1]
Ferric chloride	Red to yellow.	0·0001%.
Cobalt nitrate	Pink.	Beyond 0·00005%.
Nickel nitrate	Green.	0·0001%.
Cupric nitrate	Green-blue.	Beyond 0·00005%.
Zinc chloride	White.	Beyond 0·00005%.
Potassium alum	White.	0·001%.
Alum plus ammonium aurine tricarboxylate	Reddish.	0·001%.

[1] Sensitivity is quoted as the least percentage of tar bases (8·7% N) by volume which gave a positive test.

Because the reaction between these reagents and the tar bases involves the precipitation of the acid soluble hydroxides of the metals, they· were applicable to the detection of only the free bases and could not be applied to the acid extracts.

(2) *Acids which precipitate insoluble salts of the bases.*

This group of reagents includes many which have been used for the separation, isolation and identification of tar bases, and several " alkaloid " reagents. Because of their varied nature they are discussed separately. The sensitivities of the reagents are presented in Table 2.

TABLE 2.

Sensitivities of Reagents.

Acids which Precipitate Insoluble Salts of the Bases.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Base dissolved in acid ..	Gasoline	$0·1$ N H_2SO_4.	$0·1$ N H_2SO_4.	$0·1$ N H_2SO_4.
Chlorplatinic	0·1%	Nil	Nil	0·0001 N
Chlorauric	0·05%	Nil	0·00007 N	0·00003 N
HCl in ether	0·00005%	—	—	—
HCl (concentrated) ..	0·005%	—	—	—
Picric	0·001%	Nil	0·02 N	0·0012 N
Styphnic	0·1%	Nil	0·015 N	0·0002 N
Trinitro-*m*-cresol	0·05%	Nil	0·015 N	0·0002 N
Oxalic	0·01%	—	—	—
Tannic	0·2%	Nil	0·03 N	0·003 N
Phosphomolybdic	0·0005%	Nil	Nil	0·0002 N
Phosphotungstic	0·05%	0·003 N	0·00007 N	0·0002 N
Silicotungstic	0·005% p.p.pt. 0·00005% colour	Nil	Nil	0·002 N

The sensitivities are quoted as percentage of tar bases (8·7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(a) *Chlorplatinic Acid.* This reagent precipitates the sparingly soluble platinichlorides of the bases and has been used extensively for this purpose. It is of interest that the earliest recorded isolation and separation of the tar

bases from shale oil involved the precipitation of the bases as their platini-chlorides which were separated by fractional crystallization (Williams, 1854, 1855). The reagent was prepared by dissolving 0·0942 gm. of platinum in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. of hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(b) *Chlorauric Acid.* This reagent is sometimes used to give sparingly soluble amine salts for the separation or identification of tar bases. It was prepared by dissolving 0·1998 gm. of pure gold in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(c) *Hydrogen Chloride in Ether.* Since the hydrochlorides of the tar bases are insoluble in hydrocarbon solvents, the addition of hydrochloric acid should precipitate the chlorides, and as the precipitate would be soluble in water the sensitivity of the test should be increased by the use of an etherial solution of hydrogen chloride. The reagent was prepared by saturating redistilled ether with hydrogen chloride gas. A positive test was indicated by a yellowish or white cloudiness in the sample. An excess of reagent gave a positive test in the absence of tar bases. This test was suitable for hydrocarbon samples only.

(d) *Hydrochloric Acid (Concentrated).* This test was based on the considerations outlined in (c) above, but since it was an aqueous reagent it was not expected to be quite as sensitive. However, the reagent is always readily available and was therefore included for comparison. A positive result was indicated by a white cloudiness in the sample.

(e) *Picric Acid.* This reagent is frequently used for the isolation, separation and identification of basic organic compounds. The reagent was used in the form of the saturated aqueous solution. A positive result was indicated by the formation of a yellow precipitate or a yellow film at the gasoline-reagent interface.

(f) *Styphnic Acid.* This reagent is frequently used instead of picric acid for the same purposes and gives similar results which are no doubt due to the similarity of structure (styphnic acid is 3-hydroxy picric acid). The test was carried out as with picric acid and gave similar results.

(g) *Trinitro* m-*cresol.* This reagent (3-methyl picric acid) was included for comparison. The test was carried out as with picric acid and gave similar results.

(h) *Oxalic Acid.* The oxalates of pyridine homologues have sometimes been used for their separation and identification. The reagent was used as a saturated aqueous solution. A positive result was indicated by a white precipitate or film.

(i) *Tannic Acid.* This reagent is commonly employed as an " alkaloid " reagent, and was therefore included in this series of tests. This reagent was used as a 10% aqueous solution. The formation of a brown precipitate indicated a positive result.

(j) *Phosphomolybdic Acid.* This " alkaloid " reagent was prepared by the method of Hawke and Bergeim (1937). A positive result was indicated by the formation of a precipitate which was brown in higher concentrations and white in the lower concentrations. An excess of reagent gave a white precipitate even in the absences of the bases.

(k) *Phosphotungstic Acid.* This " alkaloid " reagent was prepared by the method of Hawke and Bergeim (1937). The test was carried out by adding two drops of the reagent to 5 ml. of the sample. A positive result was indicated by

the formation of a precipitate the colour of which increased from orange-yellow to white with decreasing tar base concentration.

(*l*) *Silicotungstic Acid.* This " alkaloid " reagent was prepared by dissolving 2 gm. of sodium tungstate in 10 ml. of hot water, adding 5 ml. of syrupy sodium silicate solution (s.g. 1·7), acidifying with 2 N nitric acid, diluting with 100 ml. of water, boiling and filtering. The clear filtrate was then acidified with 5 ml. of concentrated nitric acid. The tests were carried out using twice the usual proportion of the reagent. A positive test was indicated by the formation of a light brown precipitate or, in greater dilution, a pink colour in the gasoline sample.

(3) *Alkali salts which precipitate a salt of the base.*

(*a*) *Potassium Ferrocyanide.* This reagent is used for the detection of pyridine (Perkin, 1935) because of the low solubility of pyridine ferrocyanide. The reagent was used in the form of a saturated aqueous solution. A positive result was indicated by the formation of a white precipitate with the lower boiling bases to deep brown precipitate with the higher boiling bases.

(*b*) *Potassium Dichromate.* This reagent is commonly used for the detection of quinoline (Perkin, 1935) because of the sparing solubility of quinoline dichromate. The reagent was used in the form of a saturated aqueous solution A positive result was indicated by the formation of a yellow-orange to dark brown precipitate, the colour increasing with boiling point of the bases.

(*c*) *Potassium Triiodide.* This " alkaloid " reagent was prepared by dissolving 2 gm. of iodine and 4 gm. of potassium iodide in 100 ml. of water. A positive result was indicated by the formation of a brown precipitate.

The results of these tests are presented in Table 3.

TABLE 3.

Sensitivities of Reagents.

(*a*) Salts which precipitate a salt of the Base.
(*b*) Reagents which precipitate a double salt of the Base.
(*c*) Miscellaneous.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Bases dissolved in .. .. Reagent :	Gasoline.	$0·1$ N H_2SO_4.	$0·1$ N H_2SO_4.	$0·1$ N H_2SO_4.
Potassium ferrocyanide ..	0·5%	Nil	0·03 N	0·005 N
Potassium dichromate ..	0·01%	Nil	0·03 N	0·004 N
Potassium triiodide ..	0·05%	0·001 N	0·00001 N	0·0001 N
Mercuric chloride ..	0·05%	Nil	0·03 N	0·0002 N
Mayer's reagent	0·0005%	0·003 N	0·0007 N	0·0008 N
Dragendorf's reagent ..	0·00005%	0·0002 N	0·00001 N	0·0002 N
Sodium hydroxide ..	—	0·015 N	0·0035 N	0·0002 N
Nessler's reagent ..	0·001%	0·003 N	0·00002 N	0·000002 N

The sensitivities are quoted as percentage of tar bases (8·7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(4) *Reagents which give an insoluble double salt of the bases.*

The reagents discussed in this section could be classified in the previous section as the distinction is one of degree rather than type. The results are therefore presented with them in Table 3.

(*a*) *Mercuric Chloride.* With this reagent pyridine and quinoline and their homologues form complex mercurichlorides, usually of the form $(BHCl)_2HgCl_2$

but frequently the precipitated compound is more complex, e.g. 2·5 dimethyl pyridine gives the compound $C_7H_9N.HCl.6HgCl_2$ (Garrett and Smythe, 1902). The reagent was used in the form of a saturated aqueous solution. The formation of a precipitate indicated a positive result. With the lower boiling bases the precipitate was white, but it was more orange-brown with the crude oil bases.

(b) *Potassium Mercuric Iodide (Mayer's Reagent)*. This " alkaloid " reagent was prepared by dissolving 2·7 gm. of mercuric chloride and 10·0 gm. of potassium iodide in 190 ml. of water. A positive test was indicated by the formation of a precipitate, the colour of which was usually brown but, when near the limiting concentration of bases, was sometimes light brown, cream or even white.

(c) *Potassium Bismuth Iodide (Dragendorff's or Thresh's Reagent)*. This " alkaloid " reagent was prepared by the method outlined by Perkin (1935). A positive test was indicated by the formation of a red-orange precipitate, though the colour sometimes varied to red or brown.

(5) *Reagents which open the pyridine ring.*

The reagents discussed in this section cause the opening of the pyridine ring to give glutaconic aldehyde which forms brightly coloured Schiff's bases with primary aromatic amines.

(a) *Thionyl Chloride*. Pyridine can be converted into 4-pyridyl pyridinium chloride on heating with thionyl chloride and on treatment with alkali, this gives glutaconic aldehyde and 4-aminopyridine. Feigl and Anger (1939) developed a test which they reported to be sensitive to five γ of pyridine with a concentration limit of 1 : 10,000 by condensing the glutaconic aldehyde with α-naphthylamine. All attempts to apply this test even to the pure shale tar bases or to pure pyridine yielded negative results.

(b) *Cyanogen Halides*. Cyanogen halides react with pyridine to give the unstable N-cyano-pyridinium halide which is readily hydrolysed to glutaconic aldehyde. This reaction has been applied to the colorimetric determination of traces of cyanides (Epstein, 1947) as well as pyridine (Barta, 1935) and the detection of alkaloids containing a pyridine ring (Shmuk, 1940, 1942). In this work the three cyanogen halides were tested and the product reacted with a saturated aqueous solution of aniline or a 1% alcoholic solution of p-nitro-aniline, anthranilic acid, or α- or β-naphthylamine. The mixture was acidified and the colour change noted. The cyanogen chloride solution was prepared by adding 5 ml. of a 1% chloramine T solution to 2 ml. of a 1 N potassium cyanide solution. The cyanogen bromide and iodide solutions were prepared by adding bromine water or the potassium triiodide solution respectively to a 1 N potassium cyanide solution until there was a slight excess of the free halogen ; this was removed by the addition of a few drops of the cyanide solution. The test was carried out by shaking 5 ml. of the sample with 1 ml. of the cyanogen halide solution followed by the addition of 1 ml. of the amine solution. After the colour had been noted concentrated hydrochloric acid was added dropwise until no further change occurred. With the cyanogen chloride and bromide the tests were satisfactory, but iodine was precipitated on acidification of the tests with cyanogen iodide. The results are presented in Table 4.

(6) *Salts which give co-ordination compounds with pyridine.*

Pyridine is noted for the large number of co-ordination complexes which it forms with metallic salts, but in order that such compounds may be used for the detection of pyridine or its homologues, they should either be insoluble in or extractable from the reaction medium, and should be preferably strongly

TABLE 4.
Sensitivities of Reagents.
Cyanogen Halides and Aromatic Amines.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Bases dissolved in	Gasoline	$0 \cdot 1$ N H_2SO_4	$0 \cdot 1$ N H_2SO_4	$0 \cdot 1$ N H_2SO_4
A. Cyanogen chloride with—				
Aniline :				
Test	y. to r.br.	wh. to c.	wh. to c.	y. to c.
Sensitivity	$0 \cdot 75\%$	$0 \cdot 003$ N	$0 \cdot 000001$ N	$0 \cdot 000004$ N
p-Nitro-aniline :				
Test	y. to or.	y. to c.	y. to c.	y. to c.
Sensitivity	$0 \cdot 75\%$	$0 \cdot 015$ N	$0 \cdot 000003$ N	$0 \cdot 00001$ N
Anthranilic acid :				
Test	y. to r.br.	wh. to c.	wh. to c.	y. to c.
Sensitivity	$0 \cdot 75\%$	$0 \cdot 002$ N	$0 \cdot 000001$ N	$0 \cdot 000002$ N
α-Naphthylamine :				
Test	lt.y. to r.br.	p. to c.	y. to c.	y. to c.
Sensitivity	$0 \cdot 75\%$	$0 \cdot 003$ N	$0 \cdot 000001$ N	$0 \cdot 000002$ N
β-Naphthylamine :				
Test	y.br. to br.	m. to c.	w. to y.	br. to lt.br.
Sensitivity	$0 \cdot 00005\%$	$0 \cdot 016$ N	$0 \cdot 006$ N	$0 \cdot 00002$ N
B. Cyanogen bromide with—				
Aniline :				
Test..	y. to r.br.	Nil	cr. to c.	cr. to c.
Sensitivity	$0 \cdot 75\%$	—	$0 \cdot 00003$ N	$0 \cdot 00004$ N
p-Nitro-aniline :				
Test	y. to r.br.	y. to c.	y. to c.	cr. to c.
Sensitivity	$0 \cdot 25\%$	$0 \cdot 003$ N	$0 \cdot 00003$ N	$0 \cdot 00002$ N
Anthranilic acid :				
Test	y. to r.br.	y. to r.br.	y. to c.	cr. to c.
Sensitivity	$0 \cdot 75\%$	$0 \cdot 016$ N	$0 \cdot 000015$ N	$0 \cdot 00003$ N
α-Naphthylamine :				
Test	br. to r.br.	cr. to c.	cr. to c.	cr. to c.
Sensitivity	$0 \cdot 75\%$	$0 \cdot 0013$ N	$0 \cdot 00003$ N	$0 \cdot 00004$ N
β-Naphthylamine :				
Test	br. to lt.br.	y.br. to br.	y. to lt.y.	br. to lt.br.
Sensitivity	$0 \cdot 00005\%$	$0 \cdot 016$ N	$0 \cdot 0003$ N	$0 \cdot 00004$ N

The sensitivities are quoted as percentages of tar bases (10% N) in the gasoline sample, and as normalities in the diluted acid solutions.

Key :

br. = brown.	m. = milky.	y. = yellow.
c. = colourless.	p. = pink.	or. = orange.
cl. = clear.	r. = red.	lt. = light.
cr. = creamy.	wh. = white.	

coloured. A preliminary survey suggested that the acetates, thiocyanates and cyanates of cobalt, nickel and copper were worth investigation as they were coloured and could be extracted from the aqueous solution by chloroform (Morton, 1946). The results are presented in Table 5.

(*a-c*) *Acetates.* Since the acetates of cobalt, nickel and copper are soluble in water, and the complexes are soluble in chloroform as well as water, they could be extracted satisfactorily from the acid solutions of the bases once formed. A preliminary examination indicated that the complex was stable and could be extracted from the aqueous solution only if the pH was greater than 4. The acetate reagent was therefore prepared to act as a buffer solution as well as to provide acetate ions by dissolving 15 gm. of sodium acetate crystals and 20 ml. of glacial acetic acid in sufficient water to give 100 ml. of solution. The test was

TABLE 5.
Sensitivities of Reagents.
Co-ordination Complexes with Salts.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
	Gasoline	$0 \cdot 1$ N H_2SO_4	$0 \cdot 1$ N H_2SO_4	$0 \cdot 1$ N H_2SO_4
Bases dissolved in .. .. Salt :				
Cupric acetate	—	$0 \cdot 00025$ N	$0 \cdot 00007$ N	$0 \cdot 00025$ N
Cobalt acetate	—	$0 \cdot 00025$ N	$0 \cdot 00015$ N	$0 \cdot 00005$ N
Nickel acetate	—	$0 \cdot 0005$ N	$0 \cdot 0003$ N	$0 \cdot 00025$ N
Cupric thiocyanate ..	$1 \cdot 0\%$	$0 \cdot 003$ N	$0 \cdot 002$ N	$0 \cdot 002$ N
Cobalt thiocyanate ..	$0 \cdot 1\%$	$0 \cdot 007$ N	$0 \cdot 0008$ N	$0 \cdot 004$ N
Nickel thiocyanate ..	$0 \cdot 1\%$	$0 \cdot 003$ N	$0 \cdot 0009$ N	$0 \cdot 004$ N
Cupric carbamate (?) ..	—	$0 \cdot 001$ N	$0 \cdot 002$ N	$0 \cdot 0003$ N
Cobalt carbamate (?) ..	—	$0 \cdot 0005$ N	$0 \cdot 0001$ N	$0 \cdot 0001$ N
Nickel carbamate (?) ..	—	$0 \cdot 001$ N	$0 \cdot 003$ N	$0 \cdot 0005$ N

The sensitivities are quoted as percentage of tar bases ($8 \cdot 7\%$ N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

carried out by adding 1 ml. of this acetate reagent and $0 \cdot 5$ ml. of a 5% solution of the cobalt, nickel or cupric nitrate, and 1 ml. of chloroform, to 5 ml. of the solution of the tar bases in dilute sulphuric acid. The mixture was shaken and allowed to stand when the development of an amber colour in the chloroform layer indicated a positive test.

With pyridine the cupric acetate complex was green, but with the shale tar bases it was amber. This was first thought to be due to some impurity in the reagent but was later found to be due to the difference in the bases themselves. For comparison the tests were carried out using some pyridine which had been carefully freed from all homologues by refluxing with permanganate, and different boiling fraction of mixtures of pyridine homologues. The lower boiling homologues were obtained by fractionating denaturant grade pyridine (from coal tar) through a 12 pear column and the higher boiling fractions were obtained in previous work (Mapstone, 1947) by the careful fractionation of the shale tar bases through a 36-inch Fensko column at high reflux.

The results obtained are presented in Table 6, and indicate that the boiling range of the bases influence the colour of the complex formed. The tests were carried out on solutions containing two drops of the bases in 5 ml. of $0 \cdot 1$ N sulphuric acid.

Although pyridine gives complexes with salts of substituted acetic acids and its homologues (Morton, 1946 ; Reitzenstein, 1902, 1940), they were not included as it was felt that they would have little advantage, if any, over the acetates.

(d) *Cupric Thiocyanate.* The formation of a precipitate, $Cu(CNS)_2.2C_5H_5N$, which is soluble in chloroform to give an emerald green solution, is reported to be sensitive to $0 \cdot 05\%$ of pyridine (Morton, 1946 ; Spacu, 1922, 1923). In this work the test was carried out by adding two drops of a solution of 5 gm. of potassium thiocyanate in 10 ml. of water and two drops of a $0 \cdot 5\%$ solution of cupric nitrate to 5 ml. of the sample. This gave a black to greenish black precipitate of cupric thiocyanate. With the acid solutions the complex was extracted by the addition of 2 ml. of chloroform. A positive result was indicated by a green colour in the chloroform. With the acid samples containing the tar bases from gasoline the chloroform coagulated the dark green cupric thiocyanate precipitate and gave a yellowish-white precipitate at the interface. With the gasoline solution of the bases the black precipitate of cupric thiocyanate interfered with the observation of any colour. In this case the precipitate was

TABLE 6.

Effect of Boiling Point of Bases on Colour of Acetate Complex.

Base.	Colour of Complex in Chloroform.		
	Cobalt.	Nickel.	Cupric.
Pure pyridine	Amber.	Yellow-green.	Green.
Coal tar bases to 117° C. ..	Light yellow.	Light yellow.	Green-lemon.
„ „ 117–133° C. ..	„	„	Light green.
„ „ 133–145° C. ..	„	„	Light yellow.
„ „ 145–155° C. ..	„	„	Lemon-green.
Shale tar bases 164–170° C. ..	Very pale bluish green.	Very pale bluish green.	Very pale bluish green.
„ „ 170–180° C. ..	Yellowish green.	Yellowish green.	Yellowish green.
„ „ 180–190° C. ..	Yellowish green.	Yellowish green.	Yellowish green.
„ „ 190–200° C. ..	Yellow.	Yellow.	Yellow.
„ „ 200–210° C. ..	Yellow.	Yellow.	Yellow.
„ „ 210–212° C. ..	Greenish amber.	Greenish amber.	Amber.
„ „ ex gasoline ..	Amber.	Amber.	Amber.
„ „ ex light oil ..	Amber.	Light amber.	Amber.
„ „ ex crude oil	Amber.	Light amber.	Amber.

Remarks : The colour developed with the shale tar bases increased in intensity with increasing boiling point. The colours observed ranged through all the various shades mentioned but did not show quite as much difference as may appear to be indicated by the table.

filtered off and washed with 2-3 ml. of chloroform, the washings being collected separately. A positive test was indicated by the formation of a green colour in the chloroform washings.

(e) *Nickel Thiocyanate.* These tests were carried out as with the cupric salt using a 5% solution of nickel nitrate. With the solution of tar bases in gasoline a positive test was indicated by the formation of a green colour in the reagent and a white to green interfacial precipitate. Since the nickel thiocyanate was soluble in water the filtration step was not necessary. No precipitate was formed with the acid solutions of tar bases, but a positive test was indicated by the formation of an amber colour in the lower phase on shaking with chloroform.

(f) *Cobalt Thiocyanate.* These tests were carried out as with the cupric and nickel salts using a 5% solution of cobalt nitrate. As with the nickel salt, the cobalt thiocyanate did not precipitate and interfere with the observations of the test. With the tar bases in gasoline a positive result was indicated by the formation of a green precipitate. With the acid solutions a positive test was indicated by the formation of a greenish blue colour in the chloroform layer.

(g-i) *Cyanates (Carbamates).* The formation of the dipyridine complex of cupric cyanate has been described for the detection of copper or cyanate, the complex being soluble in chloroform to give an azure blue solution (Morton, 1946 ; Werner, 1925 ; Vogel, 1945). The complex cobalt and nickel pyridine cyanates are also soluble in chloroform (Morton, 1946 ; Davis and Logan, 1928, 1934). Since potassium cyanate is not readily available commercially, it was prepared by two different methods for comparison ; the oxidation of fused potassium cyanide with litharge, and oxidation in solution with the calculated amount of potassium permanganate. In each case the freshly prepared solution gave the same results, and in each case also the solution decomposed on standing, so that no cyanate could be detected in the reagent solution after standing for a few hours even though the test applied was sensitive to one part of cyanate in 20,000 (Vogel, 1945), although this solution still gave

colour reactions with the tar bases, of comparable sensitivity with the acetates and thiocyanates. Hydrolysis of the cyanate would give a carbamate and then a carbonate, but carbonates did not give the colour reactions. It is therefore suggested that the colour reactions observed are due to the formation of complex pyridine cupric carbamate and the corresponding cobalt and nickel salts.

The cyanate (or carbamate) reagent was prepared by adding a solution of 5·5 gm. (0·033 gm. mol) of potassium permanganate in 40 ml. of water containing 3·3 ml. (0·033 mol) of concentrated hydrochloric acid to a solution of 3·3 gm. (0·05 mol) of potassium cyanide, followed by suction filtration to remove the precipitated manganese dioxide. The object of adding the acid was to neutralize the potassium hydroxide formed during the oxidation, but it did not appear to stabilize the cyanate solution and could be omitted without effect. The test was applied to the acid solutions of the bases only, as significant results could not be obtained with the gasoline solution of the bases. The test was carried out by adding two drops of the cyanate solution and two drops of the metal nitrate solution (as for the thiocyanate tests) to 5 ml. of the sample. Dilute (5%) acetic acid was added dropwise until the precipitated (hydroxide and/or carbonate of the metal) dissolved and the complex then extracted by shaking with 2 ml. of chloroform. A positive result was indicated by the formation of a colour in the chloroform layer. With a cyanate solution that had been freshly prepared the colours obtained were : copper, light blue ; cobalt, royal blue ; nickel, pale green. If the cyanate solution had been prepared for more than half an hour the colours obtained were : copper, green to amber, depending on the boiling range of the bases ; cobalt, amber to red ; nickel, orange to brown. Because of the instability of the fresh reagent the sensitivity of the test with only the more stable hydrolysed solution was determined.

(7) Miscellaneous tests.

In this section are listed those tests that cannot be included in any of the previous categories. The results are presented in Table 3.

(a) *Sodium Hydroxide.* Addition of this reagent to an acid solution of the bases liberates the free bases. Although pyridine itself is completely miscible with water, the solubility of the homologues decreases rapidly with increasing molecular weight. The test therefore depends on the sparing solubility of the liberated mixture of the bases in water. The reagent was used as a 10% aqueous solution and a positive result was indicated by the formation of a white precipitate or white cloudiness.

(b) *Condensation with Sodium 1 : 2-naphthaquinone-4-sulphonate.* Feigl and Frehden (1934) observed that N-alkyl pyridinium compounds readily condense with 1 : 2-naphthaquinone-4-sulphonic acid to give coloured compounds. The test was carried out using methyl iodide and dimethyl sulphate as alternative alkylating agents and gave yellow to red colours with the bases. However, similar colours were obtained in the absence of the bases when the test was applied to the gasoline and sulphuric acid used to dissolve the bases. This may be due to the condensation of the sulphuric acid reagent with other reactive compounds (Erlich and Herter, 1904).

(c) *Nessler's Reagent.* This reagent is the most sensitive reagent known for the detection of ammonia and has recently been shown to be even more sensitive for the detection of aromatic secondary amines than for ammonia (Liebhafsky and Bronk, 1948). Nichols and Willits (1934) thoroughly investigated the reaction of the reagent with ammonia and concluded that the product was a colloidal suspension of the composition $NH_2Hg_2I_3$. Primary and secondary amines could therefore be expected to give the analogous products $RNH.Hg_2I_3$

and $NR_3Hg_2I_3$ respectively, and the tertiary amines may be expected to react as with Mayer's reagent. This reagent was prepared in the manner described by Perkin (1935). When tested with the heptane-octane mixture the reagent gave a slight yellow-green precipitate on standing for 10-15 seconds, in the absence of added tar bases. Because of this the sensitivity of the reagent for the detection of tar bases in gasoline solution was determined with solutions of the bases in a sample of the gasoline that had been washed with the reagent until no further precipitate was formed, and then water washed and filtered. The formation of a precipitate in the absence of added tar bases was probably due to the presence of aldehydes in the gasoline as it has been shown that Nessler's reagent can give a positive response to 1 p.p.m. of acetaldehyde in ether (van Deripe, Billheimer and Nitardy, 1936). With the solution of the bases in gasoline a positive test was indicated by the formation of a precipitate, the colour of which was usually greenish-yellow but, when near the limiting concentrations, was yellow to cream. With the acid solutions of the bases the reagent gave a white to cream precipitate.

SUMMARY.

Fixty-four different tests have been examined for their sensitivity for the detection of shale tar bases (essentially pyridine homologues). Thirty-nine of the tests are suitable for the detection of the lower boiling bases in solution in gasoline ; 26 for the detection of the bases from the gasoline in solution in dilute acid ; 33 for the detection of the bases from the light oil in solution in dilute acid ; and 36 for the detection of the bases from the crude oil in solution in dilute acid.

REFERENCES.

Barta, L., 1935. *Biochem. Z.*, 277, 412-415 ; *Chem. Abs.*, 29, 4696.
Davis and Logan, J., 1928. *J. Amer. Chem. Soc.*, 50, 2493.
———————————— 1934. *Ibid.*, 56, 2153.
———————————— 1940. *J. Amer. Chem. Soc.*, 62, 1276.
Davis and Ou, 1934. *J. Amer. Chem. Soc.*, 56, 1061.
Epstein, J., 1947. *Anal. Chem.*, 19, 272-274.
Erlich, P., and Herter, C. A., 1904. *Z. physiol. Ch.*, 41, 329. See also Feigl, F. (1939).
Feigl, F., 1939. " Qualitative Analysis by Spot Tests ", Nordemann Publ. Co., New York, 2nd English Ed., p. 347.
Feigl, F., and Frehden, O., 1934. *Mikrochemie*, 16, 79, 84. See also Feigl (1939).
Garrett, F. C., and Smythe, J. A., 1902. *J. Chem. Soc.*, 81, 449-456.
Hawke, P. B., and Bergeim, O., 1937. " Practical Physiological Chemistry ", Blakiston Co., Philadelphia, 11th Ed.
Liebhafsky, H. A., and Bronk, L. R., 1948. *Anal. Chem.*, 20, 588-589.
Mapstone, G. E., 1947. *Petroleum Refiner*, 26, 574-576.
——————————— 1948. THIS JOURNAL, 82, 85-90.
——————————— 1949. THIS JOURNAL,
Morton, A. A., 1946. " The Chemistry of Heterocyclic Compounds ", McGraw-Hill, New York, pp. 203-204.
Nichols, M. L., and Willits, C. O., 1934. *J. Amer. Chem. Soc.*, 56, 769.
Perkin, F. M., 1935. " Qualitative Chemical Analysis ", Longmans, Green and Co., London, 5th Ed.
Reitzenstein, Z., 1902. *Anorg. Chem.*, 32, 298.
Shmuk, A. A., 1940. *Piroda*, No. 2, 65 ; *Khim. Referat. Zhur.*, No. 8, 68.
——————————— 1942. *Chem. Abs.*, 36, 6308.
Spacu, 1922. *Bul. Soc. stiinte Cluj*, 1, 284.
———————— 1923. *Chem. Abs.*, 17, 1772.

van Deripe, F. N., Billheimer, E. C., and Nitardy, F. W., 1936. *J. Amer. Pharm. Assoc.*, **25**, 207-211.

Vogel, A. I., 1945. " Qualitative Chemical Analysis ", Longmans, Green and Co., London, 3rd Ed., 256-257.

Werner, 1925. *J. Chem. Soc.*, **123**, 2577.

Williams, C. G., 1854. *Phil. Mag.*, Ser. 4, 8, 209.

——————————————- 1855. *J. Chem. Soc.*, **7**, 97.

NITROGEN IN OIL SHALE AND SHALE OIL.

IX. DENSITY-TEMPERATURE RELATIONSHIPS OF SHALE TAR BASES.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

INTRODUCTION.

In working with the tar bases isolated from the gasoline obtained by the thermal cracking of crude shale oil, it was frequently found necessary to apply temperature corrections to density measurements. Since the standard correction tables for petroleum products were not applicable to the bases and no coefficient of expansion data were available, the work reported here was carried out to make up the deficiency.

BASES USED.

A quantity of tar bases were liberated by caustic soda from the hydrolysed acid sludge from the refining of the gasoline as described previously (Mapstone, 1947). Four and a half litres of the bases were distilled from a one-gallon iron pot through a twelve pear glass fractionating column. The distillate was collected in seventeen 250 ml. portions which were used for the subsequent work.

A quantity of the light recycle oil from the Dubbs cracking plant was extracted with hydrochloric acid. The bases were recovered as above and, after drying over solid caustic soda, were distilled. The distillate was used for the subsequent work.

DENSITY DETERMINATIONS.

The density of the bases was determined to four significant figures with a Westphal balance. The vessel containing the sample was well lagged so that the density of the bases could be determined over a range of temperatures. The bases were heated to 80–90° C. and poured into the sample vessel. When the rate of cooling had become steady the density was determined. By taking reasonable precautions it was possible to obtain results reproduceable within the accuracy of the test (I.P. 59/45, 1948). Several other density determinations were carried out during the 1–2 hours required for the sample to cool to about 35° C. The sample was then chilled to about 5° C. and further density determinations were carried out on it as it warmed up. A minimum of six densities were determined on each sample at different temperatures.

The density-temperature relationships were determined for only ten of the eighteen samples as the specific gravities of the remaining samples were sufficiently close to others not to warrant their being checked.

When the observed densities were plotted against the temperature, a series of straight lines was obtained (Figure 1). Two fractions of the bases (Nos. 2 and 11) had the same density within experimental error, though there was a difference of 32° C. in their mean boiling points. This also indicated that the coefficient of expansion was a simple function of the density and not of the boiling point of the sample.

COEFFICIENT OF EXPANSION.

The coefficient of expansion of each of the samples of the bases was calculated from the slope of the density-temperature curves from Figure 1. It was immediately evident that the coefficient of expansion was much higher than the corresponding figure for petroleum products and that it varied appreciably with the density of the bases. The coefficient of expansion did not give a perfect correlation when plotted against the density of the sample at 20° C. (read from Figure 1) but the results (Figure 2) indicated that the relationship was most probably linear. The method of Hanson (1947) was applied to determine the most probable correlation. This was

$$\alpha = 0 \cdot 02739 - 0 \cdot 01964 \, D_{20}.$$

where α = coefficient of expansion

D_{20} = density of bases at 20° C.
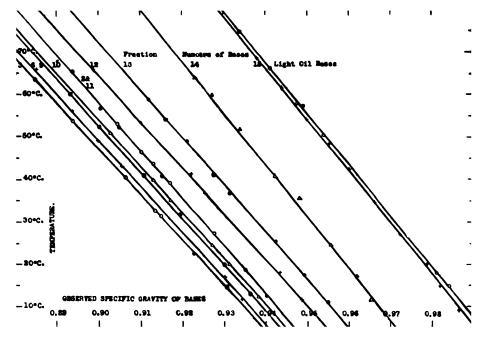
Fig. 1.—Variation of Specific Gravity of Tar Bases with Temperature.

Substituting this value of α in the usual density correction formula

$$D_t = D_{20} - \alpha(t - 20) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

where D_t = density at $t°$ C.

gives

$$D_t = D_{20} - (0 \cdot 02739 - 0 \cdot 01964 D_{20})(t - 20) \quad \dots\dots \quad (3)$$

as the overall relationship between the density and temperature for the shale tar bases. This relationship is presented in simple nomographic form in Figure 3. By means of this nomograph the density of any sample of the bases may be rapidly and simply corrected to 20° C. and, if required, calculated to any other temperature. The use of the nomograph is much simpler and more accurate than interpolation on Figure 1.

BOILING POINT-DENSITY RELATIONSHIPS.

Since the tar base fractions used to determine the density-temperature relationships were mixtures, they distilled over fairly wide temperature ranges.

For purposes of comparison, therefore, the volumetric average boiling point was calculated for each sample as the average of the temperatures at which 10%, 30%, 50%, 70% and 90% of the material had distilled under standard conditions (I.P. 28/42). The results are expressed graphically in Figure 4, which shows that, with increasing volumetric average boiling point of the bases the density first decreased and then increased.

Relatively few data are available for the density of different fractions of shale tar bases, and those that are generally apply to carefully treated fractions and cannot, therefore, be expected to be representative of the crude bases. However, Cane (1942) reported the densities of some narrow boiling fractions from shale tar bases which had not been otherwise treated and these show an increase in density with the boiling point.
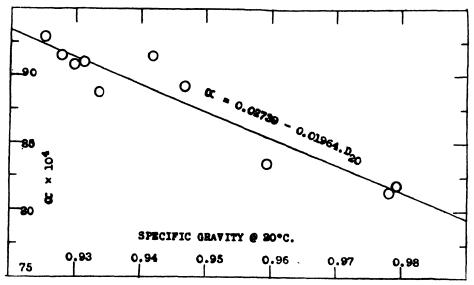
Fig. 2.—Correlation between Coefficient of Expansion and Specific Gravity of Shale Tar Bases.

The densities of alkyl pyridines, which appear to constitute the bulk of the bases, give a scatter relationship, as is to be expected, when they were plotted against the boiling points (Figure 4). By way of comparison with the unpurified bases, the data for pyridine homologues isolated from Fushun shale oil by Eguchi (1927, 1928) have been included in Figure 4. The densities recorded by Eguchi were corrected to 20° C. by means of Figure 3.

It is interesting to note that the density values for the crude tar bases lies within the spread of results for the purified bases isolated by Eguchi with the exception of the higher boiling fractions. However, the presence of a fair proportion of Eguchi's pyrindane or its homologues could readily explain the rapid increase in density with boiling point.

SUMMARY.

The variation of the specific gravity of shale tar bases with temperature has been determined and the coefficient of expansion has been correlated with the specific gravity at 20° C. The results are presented in the form of a nomograph. The specific gravity of the bases first decreases and then increases with the boiling point.
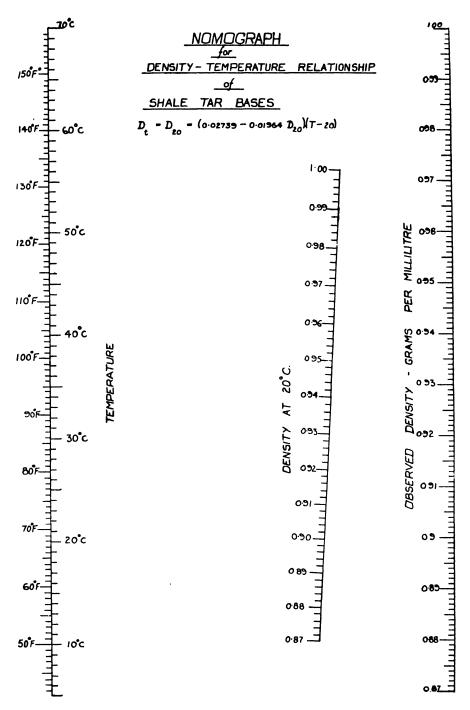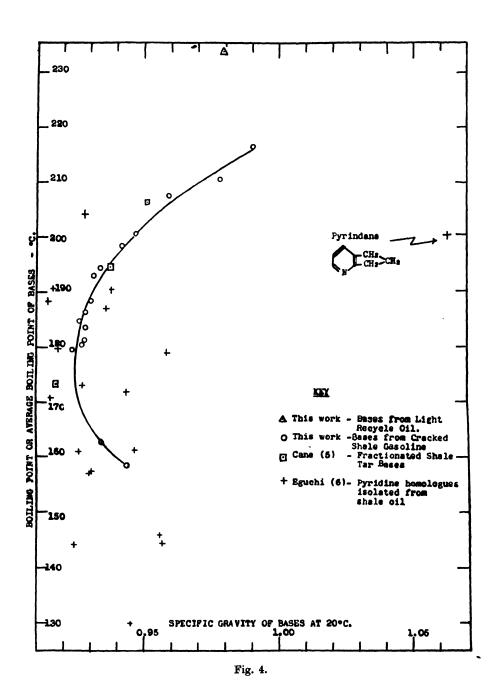
NOMOGRAPH
for
DENSITY - TEMPERATURE RELATIONSHIP
of
SHALE TAR BASES

$$D_t - D_{20} = (0.02739 - 0.01964\ D_{20})(T-20)$$

TEMPERATURE

DENSITY AT 20°C.

OBSERVED DENSITY - GRAMS PER MILLILITRE

Fig. 3.

Fig. 4.

REFERENCES.

Mapstone, G. E., 1947. " Examination of the Acid Sludge from the Treatment of Cracked Shale Gasoline ", *Petroleum Refiner*, **26**, 574-576.

I.P. 59/45, 1948. " Standard Methods for Testing Petroleum and Its Products ", *Institute of Petroleum, London*, 9th Ed.

Hanson, G. H., 1947. " Curve Fitting and Surface Fitting—Method of Least Squares ", *Petroleum Refiner*, **26**, 571-573.

I.P. 28/42, 1948. " Standard Methods for Testing Petroleum and Its Products ", *Institute of Petroleum, London*, 9th Ed.

Cane, R. F., 1942. " The Nitrogen Bases in Tasmanite Shale Oil ", *Pap. and Proc. Roy. Soc. Tasmania*, 55-61.

Eguchi, T., 1927. *Bull. Chem. Soc. Japan*, **2**, 176 ; *Chem. Zentr.*, **2**, 1223.

———————— 1928. *Bull. Chem. Soc. Japan*, **3**, 227-234, 235-243 ; 1929. *Chem. Zentr.*, **1**, 330, 331.

OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1948.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times, either for personal effect, or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the *Nautical Almanac* for 1938 and the reduction completed by the method given there. The necessary data were taken from the *Nautical Almanac* for 1948, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

TABLE 1.

Serial No.	N.Z.C. No.	Mag.	Date.		U.T.	Observer.
					h m s	
164	429	6·9	Mar.	15	8 47 41·0	R
165	996	6·8	Apr.	15	8 13 24·1	W
166	1424	6·8	Apr.	18	10 25 56·3	W
167	1621	7·5	May	17	7 34 40·5	R
168	1864	6·8	May	19	12 18 28·3	R
169	1869	6·1	May	19	13 46 32·9	W
170	1598	6·4	June	13	9 51 11·9	W
171	2025	6·8	July	14	9 22 31·8	R
172	2228	5·9	Aug.	12	9 32 02·8	W
173	2398	6·1	Aug.	13	14 44 55·2	W
174	1946	7·2	Sept.	6	9 34 58·3	R
175	—	7·7	Sept.	6	9 41 06·1	R
176	2069	7·3	Sept.	7	10 21 41·7	W
177	2189	7·0	Sept.	8	9 13 10·4	R
178	2479	5·3	Sept.	10	11 25 02·6	R
179	2480	5·3	Sept.	10	11 25 15·8	R
180	2482	6·7	Sept.	10	11 46 10·4	R
181	2634	7·4	Sept.	11	12 21 55·4	W
182	2650	4·7	Sept.	11	14 36 51·7	W
183	2796	6·8	Sept.	12	12 11 46·0	W
184	3175	4·8	Sept.	15	11 08 35·0	W
185	3265	6·6	Oct.	13	10 42 10·0	R
186	3106	5·4	Nov.	8	13 40 17·2	R

Table 1 gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1948). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table 2 gives the results of the reductions

TABLE 2.

Serial No.	Luna-tion.	p	q	p^2	pq	q^2	$\triangle\sigma$	$p\triangle\sigma$	$q\triangle\sigma$	Coefficient of $\triangle\alpha$	$\triangle\delta$
164	312	+ 90	+ 43	81	+39	19	−1·6	−1·4	−0·7	+ 9·7	+ 0·73
165	313	+ 99	−12	99	−12	1	−0·3	−0·3	0·0	+13·1	−0·11
166	313	+ 99	−15	98	−15	2	−0·2	−0·2	0·0	+12·4	−0·47
167	314	+ 80	+ 60	64	+48	36	−2·3	−1·8	−1·4	+14·3	+0·21
168	314	+ 89	+ 46	79	+41	21	−1·5	−1·3	−0·7	+15·0	0·00
169	314	+ 98	+18	97	+18	3	−1·5	−1·5	−0·3	+14·4	−0·29
170	315	+ 87	−50	75	−43	25	−0·7	−0·6	+0·4	+ 8·5	−0·82
171	316	+ 92	+40	84	+37	16	−1·7	−1·6	−0·7	+14·7	−0·02
172	317	+ 94	−34	88	−32	12	−0·1	−0·1	0·0	+11·0	−0·62
173	317	+ 27	+96	7	+26	93	−1·0	−0·3	−1·0	+ 6·3	+0·89
174	318	+100	+ 4	100	+ 4	0	−0·6	−0·6	0·0	+13·5	−0·41
175	318	+ 99	+17	97	+17	3	−1·3	−1·3	−0·2	+14·1	−0·29
176	318	+ 84	−55	70	−46	30	+1·4	+1·2	−0·8	+ 8·0	−0·84
177	318	+ 81	+58	66	+47	34	−1·7	−1·4	−1·0	+13·6	+0·27
178	318	+ 74	−68	54	−50	46	+0·2	+0·1	−0·1	+ 8·5	−0·77
179	318	+ 73	−68	53	−50	47	+0·6	+0·4	−0·4	+ 8·4	−0·78
180	318	+ 90	−44	81	−40	19	0·0	0·0	0·0	+11·1	−0·56
181	318	+ 98	−19	96	−19	4	−1·0	−1·0	+0·2	+13·0	−0·22
182	318	+ 34	+ 94	12	+22	88	−1·4	−0·5	−1·3	+ 4·7	+0·93
183	318	+ 99	−15	98	−15	2	−1·0	−1·0	+0·2	+13·3	−0·06
184	318	+ 99	−16	97	−16	3	−0·1	−0·1	0·0	+13·9	+0·19
185	319	+ 98	−20	96	−20	4	−1·7	−1·7	+0·3	+14·1	+0·19
186	320	+100	+ 8	99	+ 8	1	−1·0	−1·0	−0·1	+12·9	+0·39

which were carried out in duplicate.   The N.Z.C. numbers given are those of the Catalog of 3539 Zodiacal Stars for the Equinox 1950·0 (Robertson, 1940), as recorded in the *Nautical Almanac*.

The star involved in occultation 175 was not included in the *Nautical Almanac* list ; it is G.C. 18326 (apparent place R.A. 13ʰ 30ᵐ 44ˢ·10, Dec. −8° 10′ 14″·0).

REFERENCES.

Robertson, A. J., 1940.   Astronomical Papers of the American Ephemeris, **10**, Part II.
Robertson, W. H., 1948.   THIS JOURNAL, **82**, 25.   Sydney Observatory Papers, No. 5.

PROCESSES IN DIELECTRICS CONTAINING FREE CHARGES.

THE ENTROPY OF ELECTROSTATIC SYSTEMS.

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I. INTRODUCTION.

The dielectric behaviour of a space can be described in terms of its permittivity and conductivity, which then can be combined in a complex dielectric "constant" ε. The permittivity, given by the real part of ε, is a measure of the free electrostatic energy, which is available for doing reversible work, and is stored in the dielectric. The conductivity, which can also be expressed in terms of the dielectric loss angle $\tan \delta$, to which it gives rise, is a measure of the degree of how far the energetic state of the dielectric under applied electric stress is a state of labile equilibrium, i.e. how much energy must be expended in order to maintain that equilibrium state.

In an ideal vacuum condenser, all the energy stored in the field can be recovered without loss : it is free electrostatic energy, capable of doing reversible work. If the dielectric is filled with a polarizable substance, but still imagined loss-free, the energy stored will be greater depending on the permittivity of the substance, but it will still remain free electrostatic energy which can be reversibly recovered without loss.

Dielectric losses can arise from two fundamentally different causes : firstly, due to imperfections and losses in the polarization process, i.e. by the necessity for the expenditure of energy for the alignment and dealignment of the atoms and/or molecules, and secondly, due to the presence of free charges in the dielectric. A very considerable amount of study has been devoted to polarization losses. It is the purport of the present paper to investigate theoretically the influence of a space-charge in a dielectric on its dielectric behaviour.

II. ANALYSIS.

An ideal vacuum condenser, of capacity C_{vac}, one plate of which is charged to a potential V with reference to the other plate, has stored free electrostatic energy W_f (capable of doing reversible work), and is given by

$$W_f = |\, V^2 C_{\text{vac}}/2 \,| \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

The sign of W_f depends on the point of view : following usual thermodynamic convention, it will be taken as negative if work equal to W_f can be done reversibly *by* the system.

If now the vacuum is filled with any material medium, V being maintained at its previous value, the quantity of free energy stored will be altered. It is therefore possible to define the electrostatic capacity of a system from equation (1) :

$$C = 2W_f/V^2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

The permittivity of the dielectric, or the real part of ε, will then be given by

$$\varepsilon' = C/C_{\text{vac}} = D \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

Considering now a plane parallel condenser of unit area, whose plates are separated by a distance a and connected by resistance-less leads to a source of $EMF = V$: when the dielectric between the plates is a loss-free medium of permittivity D, the work done in charging the plates is W_0. Because the dielectric is loss-free, all the energy W_0 then is free energy stored in the dielectric.

If now a space distribution of charges of local density $\rho = f(x)$, where x refers to a variable point in the dielectric x cm. distant from one plate, is introduced into the dielectric (the potential difference across the condenser being maintained at the previous value V), additional work W_e will be necessary in order to do so. W_e will be stored in the condenser above and additional to the work W_0 done in charging the loss-free condenser. The total energy stored in the condenser, W_t, is thus given by

$$W_t = W_0 + W_e \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

However, not all the energy W_t stored in the condenser which now contains free charges in its dielectric, will be free energy, since a quantity of energy W_φ will be bound in the space charge itself. The total energy W_t, therefore, can be written as the sum of the free electrostatic energy W_f which is available for reversible work, and the unavailable energy bound within the space charge itself, W_φ:

$$W_t = W_f + W_\varphi \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

It should be stressed again that the potential difference across the condenser is maintained at a constant value V throughout the above operations. Combining equations (4) and (5) yields for W_f

$$W_f = W_0 + W_e - W_\varphi \quad \dots\dots\dots\dots\dots\dots\dots\dots (6)$$

The work W_e is done against V:

$$W_e = -VD(E'_a - E_0)/4\pi \quad \dots\dots\dots\dots\dots\dots\dots (7)$$

where E'_a is the total field existing in the presence of the space-charges at the plate which is maintained at the potential V against the other plate. E_0 is the Laplacian field in the absence of a space charge, given by

$$E_0 = -V/a \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

If a field E' is produced at a point x by the space charges, the energy bound within a space configuration of charges can be written

$$W_\varphi = \frac{D}{8\pi} \int_0^a (E')^2 dx \quad \dots\dots\dots\dots\dots\dots\dots\dots (9)$$

Furthermore

$$dE'/dx = 4\pi\rho/D \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (10a)$$

$$\int_0^a \rho\, dx = Q, \text{ the total charge/cm.}^2 \quad \dots\dots\dots\dots\dots (10b)$$

The energy equation for the condenser containing free charges in its dielectric thus follows as

$$W_f = -\left[C_0 V^2/2 + VQ + \frac{D}{8\pi} \int_0^a (E')^2 dx \right] \quad \dots\dots\dots\dots\dots (11)$$

where C_0 stands for the geometric capacity of the condenser in the absence of space charges, given by

$$C_0 = D/4\pi a = 2W_0/V^2 \quad \dots\dots\dots\dots\dots\dots\dots (12)$$

In any actual case the term VQ in equation (11) will always be negative, since either V or Q will have to be negative, in order to maintain the space charge. The negative sign of W_f in equation (11) indicates that work equal to W_f can be done reversibly *by* the system.

From equation (11) the capacity and the permittivity of the charge filled dielectric follow by virtue of equations (2) and (3), once the field distribution within the dielectric is known. It is seen that the presence of a space charge leads to a diminution of the effective dielectric constant of the medium, a well known experimental fact which has been proved, e.g. for ionized gases, by Imam and Khastgir (1937). In the appendix, C and the effective dielectric constant D are calculated for a simple but representative case, viz. a plane parallel diode obeying the Child-Langmuir 3/2 power law. D results as 3/5, a value which has been obtained, *inter alia*, by Llewellyn (1941) from dynamical considerations. Another interesting case in point is the electric double layer confronting a polarized electrode in an aqueous solution. C_0 is negligibly small in this case, since the whole condenser comes into being only by virtue of the ionic space charge. This problem will be dealt with in a separate communication.

As W_f represents free energy capable of doing reversible work, the laws of thermodynamics are applicable, if a one-to-one correspondence can be established between a given electrical and a thermal system having the same free energy G, so that $G = W_f$. The Gibbs Free Energy G is given by

$$G = U + W - TS \dotfill (13)$$

where U is the internal energy of the system, W the work done on the system, T the absolute temperature and S the entropy.

A thermal system where $G = W_f$ can be constructed as follows :

Given a canonical distribution of elementary condensers each charged to a certain potential ψ and having an average density of charge $\bar{\rho} = $ Const., so that the total charge Q is also constant : following the standard statistical treatment (Lindsay, 1941) the entropy of the system is defined in terms of the distribution modulus θ, which has the dimension of energy and can be interpreted as the average energy of every unit cell making up the statistical ensemble. In the case of a thermal system, these unit cells are particles (say gas molecules) with an average energy of $kT/2$, measured in thermal units. In the case of an electrical system, the average energy equals $\bar{\rho}\psi/2$, measured in electrical units, and each cell represents one elementary condenser. Integrating over the whole system, its energy becomes equal to $QV/2$, where V is the potential appearing across the plates of the resulting macroscopic condenser, while the energy of the thermal system becomes equal to $RT/2$. As the energy of the electrical and that of the corresponding thermal system are equal, it follows that[1]

$$QV = RT = \theta \dotfill (14)$$

An ideal gas is characterized by

$$C_p - C_v = \text{Constant} = R \dotfill (15)$$

The gas law $pv = RT$ then holds, C_p and C_v being the specific heat at constant pressure and constant volume, respectively, and p the pressure and v the volume. This is the equivalent to the restriction imposed on the electrical system by the condition that $Q = $ Constant. If $Q \neq$ Constant, the electric system corresponds to a non-ideal gas where equation (15) no longer holds, i.e. where $R = f(T \dots)$.

Equation (14) shows that appropriate values have to be assigned to V and T, because Q and R (for an ideal gas and its electric counterpart) are constants. Therefore, if V is given, T is uniquely determined, and *vice versa*. A one-to-one correspondence thus exists between these two quantities.

An analogue between V and T has first been proposed by Mach (1871, 1919) and Lippmann (1876). The electric-current thermal-current analogue is well known (Avrami and Paschkis, 1942) and recently Bosworth (1946) has established the thermal equivalent of the Ohm, Farad and Henry.

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[1] Equation (14) in the form $V^2C/2 = kT/2$ has been first used by Einstein (1907) in a treatment of the effect of Brownian motion on the potential across a condenser.

The one-to-one correspondence between V and T having been established, it also follows from equation (14) that $Q = \int_0^a \rho\, dx$ corresponds to R. The product $RT = pv$ thus corresponds in the electrical case to W_e.

As to the enthalpy H, the counterpart of the total energy W_t of the electrical system, it can be written

$$H = U + W \quad \dotfill \quad (16)$$

Since it has been shown that $W = pv = RT$ corresponds to $W_e = QV$, U is seen to be in one-to-one correspondence with W_0, since the electric and the corresponding thermal system are to have equal energy. W_0 electrically also behaves similarly to U in a cyclic process, because it returns to its initial value when V (or T in the thermal case) is first increased and then allowed to return to its former value. In other words, the internal energy in the thermal case is a single valued function of T exactly as the energy stored in the geometric capacitance of a condenser is a single valued function of the potential to which it is charged. It is now seen that the term TS in the thermal case, equation (13), corresponds to the term W_φ in the electric system described in equation (6). Since T has been shown to be in one-to-one correspondence to V, the quantity W_φ/V, which it is proposed to call the ELECTRICAL ENTROPY, similarly corresponds to the thermal entropy S. More accurately, the differential change in the electrical entropy dS_e, defined by

$$dS_e = \frac{dW_\varphi}{V} \quad \dotfill \quad (17)$$

is in one-to-one correspondence to the entropy element

$$dS = \frac{dq}{T} \quad \dotfill \quad (18)$$

For a rigid proof that equation (17) represents an entropy element it must be shown (1) that dW_φ is not an exact differential, and (2) that $1/V$ is an integrating factor making dW_φ/V exact.

Since W_φ is a function of V, $\oint W_\varphi dV$ would vanish if dW_φ were exact. From equations (4) and (5) W_φ can be written

$$W_\varphi = W_t - W_f \quad \dotfill \quad (19)$$

If $\oint W_\varphi dV = 0$ would hold, $\oint W_t dV$ would vanish also, since $\oint W_f dV$ vanishes by definition of W_f as free energy available for reversible work. But in general

$$\oint W_t dV \neq 0 \quad \dotfill \quad (20)$$

since work might be done on or by the system. Therefore contention (1) is proved.

As to the second proposition, it must be shown that

$$\oint \frac{dW_\varphi}{V} = 0 \quad \dotfill \quad (21)$$

Again, since $\oint W_f dV = 0$, equation (21) can be written, using equation (5), thus :

$$\oint \frac{W_e}{V} dV = 0 \quad \dotfill \quad (22)$$

Assume that this were not true. It then would be possible by repeating the cyclic process of first increasing and thereafter decreasing V to its initial value, to increase the total space charge Q without limit (always assuming the potential changes to be slow compared with the relaxation time of the process, or in other words slow enough to allow the charge distribution to come into equilibrium for all intermediate values of V). This would be against experience and against the laws of thermodynamics. The proposition, therefore, is proved.

The electrical entropy of an electrostatic system where Q =constant follows directly from the statistical considerations on page 68 and equation (14), as

$$(S_e)_{Q-\text{const}} = Q \log (V/N!) \quad \dots\dots\dots\dots\dots\dots\dots\dots (24)$$

where N is the number of unit cells comprising the statistical ensemble, and therefore an additive constant. Equation (24) is thus seen to be formally identical with the Boltzmann relation

$$S = k \log w + \text{const} \quad \dots\dots\dots\dots\dots\dots\dots\dots (25)$$

where w is a measure of the probability of the system to be found in a state determined by the energy of the statistical canonical distribution modulus θ.

Furthermore, it is seen that the electrical entropy thus comes within the scope of definition of entropy as a measure of the extension of an equilibrium state, as given by Postma (1916). Equation (24) can also be derived from equation (17), which can be written

$$dS_e = \frac{1}{V} \frac{dW_\varphi}{dV} dV \quad \dots\dots\dots\dots\dots\dots\dots\dots (26)$$

for $Q = dW_\varphi / dV = $ Constant.

Table 1 lists the two sets of quantities shown to be in one-to-one correspondence with each other:

TABLE 1.

Electrical Quantity.	Thermal Quantity.
Free electrostatic energy W_f.	Gibbs' free energy G.
Energy stored in condensor in the absence of space charges, W_o.	Internal energy U.
Work done in introducing the space charges, W_e.	Work done by or against external forces, W.
Potential V.	Temperature T.
Volume of the condenser v.	Volume of the gas v.
Energy bound in the space charge, W_φ.	TS.
The product potential V by average space charge density ρ.	Average pressure of the gas, $\bar{p}$.
Total energy W_t.	Enthalpy H.
Total charge $Q = \int \rho dv$.	Gas constant $R = C_p - C_v$.
Electrical entropy dW_φ/V.	Entropy dq/T.

All the electrical quantities are time-variable to the extent that V is a function of time. Moreover, if a cyclic process is considered by first increasing V to a predetermined value and then reducing it again to its initial value, then the time taken for such a cycle must be large compared with the relaxation time of the readjustment of the system to the altered field. This is the exact counterpart to the thermal case where in an isochoric cycle the change of T must not be too fast for the thermal conductivity of the gas. In both cases, the rate of change of T or V, respectively, must be sufficiently small to permit consideration of the whole gas or dielectric as in a state of thermal or electrical equilibrium for every intermediate value of T or V. Since the temperature T represents an absolute, irreducible, dimensional quantity which enters into the dimensions of thermal quantities, it is clearly impossible to bring all thermal and the corresponding electric units to the same dimensions. The electric quantities, in the electrostatic system, are based upon the permittivity of free space, which enters into their dimensional formulae and which equally represents an absolute and irreducible dimensional quantity. However, there are some cases where the corresponding electric and thermal quantities also have the same dimension, even if that cannot

be expected in general. The pressure $\bar{p}$ and $\bar{\rho}V$ present such an exceptional case, having the same dimension $(ml^{-1}t^{-2})$.

The second law of thermodynamics can now be applied to a purely electrical system :

EVERY PURELY ELECTRICAL PROCESS WILL TAKE PLACE IN SUCH A MANNER THAT THE ELECTRICAL ENTROPY OF THE SYSTEM INCREASES.

This can take place either by the increase of the bound energy W_φ, by the decrease of the potential difference V, or by a combination of both processes. Moreover, in correspondence to the thermal case, $dS_e = V^{-1}dW_\varphi$ is an exact differential and the electrical entropy completely and uniquely describes the electrical state of the system.

The following examples might serve to illustrate the application of this law :

    (i) A SOLID DIELECTRIC UNDER ELECTRIC STRESS HIGH ENOUGH TO PRODUCE IONIZATION :

        Once ionization sets in, i.e. free charges appear, the dielectric constant of the medium decreases (Imam and Khastgir, 1937) (W_φ increasing and W_f therefore decreasing). At the same time the conductivity of the dielectric increases (the potential V across it is lowered unless maintained from outside), as is well known.

    (ii) A REVERSIBLE ELECTRODE REACTION :

        Increase of concentration of dischargeable ions (i.e. increase of free charges) reduces the discharge potential (V decreases). At the same time a higher potential is needed before the limiting current is reached because a greater proportion of the energy supplied, W_t, is transformed into unavailable energy W_φ. Both effects are well known experimental facts (Kolthoff and Lingane, 1941).

The entropy of a perfect monatomic gas is given by

$$S = \frac{5}{2}R \ \log \ T - R \ \log \ \bar{p} + \text{Const.} \ \dots\dots\dots\dots\dots (27)$$

In the corresponding electrical system this becomes, by virtue of equivalences listed in Table 1,

$$S_e = \frac{5}{2}Q \ \log \ V - Q \ \log \ \bar{\rho}V + \text{Const.} \ \dots\dots\dots\dots (28)$$

$$= \frac{3}{2}Q \ \log \ V - Q \ \log \ \bar{\rho} + \text{Const.} \ \dots\dots\dots\dots (29)$$

The average charge density $\bar{\rho}$ in the electrical counterpart of a perfect gas being constant (see page 68, equations (14) and (15) and following), equation (29) can be expressed thus :

$$S_e = \frac{3}{2}Q \ \log \ V + \text{another constant} \ \dots\dots\dots\dots (30)$$

A monatomic gas having three degrees of freedom, the electrical entropy of the corresponding electrical system, *per degree of freedom*, results as

$$S_{e/f} = \frac{Q}{2} \ \log \ V + \text{Constant} \ \dots\dots\dots\dots (31)$$

However, the space charge element in a plane parallel condenser has only two degrees of freedom of translatory motion, which also follows from Gibb's Phase Rule : If C is the minimum number of components required to describe each phase of the system completely and P is the number of phases, the degrees of freedom F are given by

$$F = C - P + 2 \ \dots\dots\dots\dots\dots\dots (32)$$

Thus in the electric system $P=2$, corresponding to free energy and bound energy and C is equal to 2, corresponding to the charge and the potential, describing each phase. F therefore equals 2. The total electrical entropy of an electrical system where $Q=$ Constant, therefore follows as

$$S_e = Q \ \log \ V + \text{Constant} \quad \dotsi \quad (33)$$

This equation thus has been derived from purely thermodynamical considerations by application of the one-to-one correspondences listed in Table 1. As can be seen, equation (33) is identical with equation (24), which was derived directly from the statistics of the electrical system. This, then, is an example for the correctness of applying thermodynamic reasoning to electrical processes.

If the potential V on one plate of the condenser is reduced to another value V', a certain amount of energy W_φ will not appear as available energy, but will be dissipated or irreversibly expended. In parallelism to a thermal process, W_θ can be calculated from the electrical entropy S_e:

$$W_\varphi = V' \int_{V'}^{V} \frac{1}{V} dW_\varphi = V' \int_{V'}^{V} F\left(x, \ V, \ \frac{dV}{dx}\right), \ dx \quad \dotsi \quad (34)$$

It is of interest to find some conditions which make W_θ vanish or a minimum $\neq 0$. It is obvious that if $W_\theta = 0$ or $V' = 0$, W_θ also will vanish. The former case is trivial, since it amounts to a condenser without space charge. The latter can be realized only by connecting the condenser plates for a time sufficient to allow *complete* discharge. It is known, however, from the phenomenon of dielectric absorption that the rate of decay of W_φ in general even after the removal of V is slow (Gross and Denard, 1945). To find the conditions which make W_θ a minimum $\neq 0$, Euler's equation is set up for the path which makes the integral in equation (34) a minimum :

$$\frac{\partial^2 F}{\partial \rho \partial x} + \frac{\partial^2 F}{\partial V \partial \rho} \frac{dV}{olx} + \frac{\partial^2 F}{\partial \rho^2} \frac{d^2 V}{dx^2} = 0 \quad \dotsi \quad (35)$$

where $F = F\left(x, \ V, \ \frac{dV}{dx}\right)$ and $p = -dV/dx$. In the present case, $F = \frac{(E')^2}{V}$

and $p = -dV/dx = (E' + E_0)$. It is seen that $F =$ Const. is one solution of equation (35). This is the special case of a dielectric where

$$(E')_a = \frac{4\pi Q}{D} = \text{Const.} \ V^{\frac{1}{2}} \quad \dotsi \quad (36)$$

The connection between this condition and the well-known Debye-Hueckel equation will be dealt with in a separate communication.

Another solution of equation (35) is $p =$ Constant :

$$dV/dx = \text{Constant}$$
$$V = \text{Const.}x + \text{Constant} \quad \dotsi \quad (37)$$

i.e. a linear relationship between local potential V and x, or, therefore, the condition that the *total* potential is Laplacian. The system thus will operate under minimum energy dissipation if the externally applied field E_0 and the field due to the space charges cancel at the condenser plates, i.e. when the system is in potential equilibrium at the plates. This is possible only in a region of space charge where $E_0 = -4\pi Q/D$. This is equivalent to $dQ/dV =$ Const., which plays a similar role to the specific heat in thermal processes. For the reversibility of the electric process, therefore, it is sufficient if the *total* space charge present is either constant or linearly proportional to the potential across the condenser. This condition does not imply a purely static case, i.e. the absence

of a space-current : it suffices if div $(\partial \rho / \partial t)$ is either constant or linearly proportional to V. In other words, a dielectric may contain free charges and still be loss-free, subject to the above conditions. Physically, these can be interpreted as meaning that for minimum electrical waste energy the field at the plate must be in equilibrium with the field of all space charges in the dielectric. Such systems actually exist in nature ; they are approached in electro-chemical reactions, in the region in front of the plate (or in the space between plate and suppressor) of a pentode, where the plate current is nearly independent of the plate potential, and also by a triode biased to cut-off, so that the field due to the grid, plate and electrons exactly balance.

The capacity defined in equation (2) represents the *d-c* capacity measurable after a steady state has been attained. For varying and for alternating potentials a capacity C_d is defined by the differential

$$C_d = dq_0/dV$$
$$q_0 = 2W_f/V \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (38)$$

q_0 being the free charge. Since the derivative dQ/dV enters into the expression for C_d, it is seen that the *change* in the free energy and with it C_d, depend on the relaxation time of Q. In other words, the ideally reversible free charge is truly so only for infinitely small (i.e. infinitely slow) changes of V, since it will always take a finite time for Q to adjust itself to a change in V. This time, as has been pointed out by Gross and Denard (1945), may be extremely long, in some cases even hundreds of thousands of years. It is another example of processes, so well known to thermodynamics and chemical kinetics, processes which are only partly reversible in practice, while in themselves they are inherently completely reversible reactions.

III. SUMMARY.

The free electrostatic energy, capable of doing reversible work, stored in a space-charge filled condenser, is calculated, yielding an expression for the effective dielectric constant of a medium containing free charges.

A one-to-one correspondence between a number of thermal and electrical quantities is established. The electrical entropy S_e is defined as $dS_e = V^{-1}dW_\varphi$, V being the potential difference across the condenser and W_φ the energy bound within the space configuration of charges. It is proved that dS_e is an exact differential. The second law of thermodynamics is applied to purely electrical systems in the form : Every purely electrical process will take place in such a manner that the electrical entropy of the system increases.

Further equivalences between electrical and thermal processes are demonstrated. It is shown that a space charge filled condenser may still be loss free, if the sum total of the free charges in its dielectric is constant or linearly proportional to the potential difference across the condenser.

IV. ACKNOWLEDGEMENTS.

V. APPENDIX.

The Child-Langmuir 3/2 power law for a plane parallel diode can be written thus (Koller, 1937) :

$$V = \left[\frac{Jx^2 9\pi}{(2e/m)^{1/2}} \right]^{2/3} \quad \dots\dots\dots\dots\dots\dots\dots (39)$$

where J is the space current density, x a variable point where a local potential V exists (at the plate, $x=a$, the interelectrode spacing and $V=V_0$ the plate voltage), and e/m the specific electronic charge. The space charge being *in vacuo*:

$$\frac{D}{8\pi}\int_0^a (E')^2 dx = \frac{1}{8\pi} \frac{16\pi(9\pi)^{1/3}J^{4/3}a^{5/3}}{(2e/m)^{2/3}} \frac{3}{5} \quad \dots\dots\dots\dots\dots (40)$$

Since

$$\rho = V/v = \frac{JV^{-1/2}}{(2e/m)^{1/2}} \quad \dots\dots\dots\dots\dots (41)$$

where v is the average local velocity of the electrons, given by

$$mv^2/2 = eV \quad \dots\dots\dots\dots\dots\dots\dots (42)$$

Q results as

$$Q = \int_0^a \rho dx = \frac{J}{(2e/m)^{1/2}}\int_0^a V^{-\frac{1}{2}} dx \quad \dots\dots\dots (43)$$

But from equation (39):

$$V^{-1/2} = \left[\frac{Jx^2 9\pi}{(2e/m)^{1/2}}\right]^{-1/3} \quad \dots\dots\dots\dots\dots (44)$$

Therefore

$$Q = \frac{J}{(2e/m)^{1/2}}\int_0^a \left[\frac{9\pi J}{(2e/m)^{1/2}}\right]^{-1/3} x^{-2/3} dx \quad \dots\dots (45)$$

yielding on integration

$$Q = \frac{J^{2/3}3a^{1/3}}{(9\pi)^{1/3}(2e/m)^{1/3}} \quad \dots\dots\dots\dots\dots (46)$$

Recalling equations (2), (11) and (12) for C, W_f and C_0 respectively, it follows on substitution that

$$D = C/C_0 = -1 + \frac{8}{3} - \frac{16}{15} = \frac{3}{5} \quad \dots\dots\dots\dots (47)$$

VI. REFERENCES.

Avrami, M., and Paschkis, V., 1942. *Trans. Amer. Inst. Chem. Engrs.*, **38**, 631.

Bosworth, R. C. L., 1946. *Phil. Mag.*, **37**, 803.

Einstein, A., 1907. *Ann. d. Physik*, IV-22, 569.

Gross, B., and Denard, L. F., 1945. *Phys. Rev.*, **67**, 253.

Harper, D. R., 1928. *J. Wash. Acad. Sci.*, **18**, 459, *et al.*

Imam, A., and Khastgir, S. R., 1937. *Phil. Mag.*, **23**, 858.

Koller, L. R., 1937. " Physics of Electron Tubes ", McGraw Hill Inc., New York, p. 108.

Kolthoff, I. M., and Lingane, J. J., 1941. " Polarography ", Interscience Publ. Inc., New York, p. 147.

Lindsay, R. B., 1941. " Introduction to Physical Statistics ", J. Wiley and Sons, New York.

Lippmann, G., 1876. *Comptes R.*, **82**, 1425.

Llewellyn, F. B., 1941. " Electron Inertia Effects ", Cambridge University Press.

Mach, E., 1871. " Lotos ", February.

————— 1919. " Prinzipien der Waermelehre ", Leipzig, 3rd Ed.

Postma, O., 1916. *Kon. Akad. Wetenschapp. Amsterdam Proc.*, 18·7, 1048.

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THE EFFECT OF pH UPON THE ULTRA-VIOLET ABSORPTION SPECTRA OF PYRIDINE TYPE COMPOUNDS.

By L. E. LYONS, B.A., M.Sc.

INTRODUCTION.

Previous studies by Loofbourow and Stimson (1940) and Craig and Short (1945) have shown that the ultra-violet absorption of such N-containing substances as barbituric acid, guanine, adenine and the various aminoacridines changes with pH. An explanation for the former group has been given in terms of tautomers and for the second in terms of ions.

The present study was undertaken with a view to determining the molecular species present at different pH's, to assist in the interpretation of polarographic curves, but the results may be of interest to those concerned in the theoretical investigation of the energies of molecular π-orbitals, as the introduction of H^+ into, say, pyridine adds no electrons and gives a resultant molecule which in some ways resembles benzene, having a similar distribution of nuclei :

The difference from benzene is twofold : (i) the symmetry of the molecule is lessened by the presence of N instead of a C ; and (ii) an excess positive charge is present. The effect of (i) would be expected as a blurring of the vibrational partial band structure and of (ii) as an alteration in the energies of the molecular orbitals, necessitating different values given to certain integrals in the theoretical treatment, and being revealed in a shift in the wave number of the corresponding band. Furthermore, it was thought possible that the results might throw some light on vibrational modes of the free base molecules.

EXPERIMENTAL.

All measurements were made on a Beckmann ultra-violet spectrophotometer with a hydrogen discharge lamp as light source. Each substance used was dried and purified by either repeated fractionation or crystallization.

The strength of all solutions was 10^{-4} M.

RESULTS.

The results are graphed and tabulated, together with some values in hydrocarbon solvents obtained from the literature.

ε is defined by the relation $I = I_0 10^{-\varepsilon cd}$

where I, I_0 are transmitted and incident light intensities,

    c is molar concentration,

    d is cell thickness (cm.).

DISCUSSION OF RESULTS.

1. The formation of the $\equiv NH^+$ ion at pH 4 from the free base, $\equiv N$, is consistent with the results, as will be seen from the following ; which means that the absorption at the lower pH is in every case by a molecular species different from that which absorbs at pH 7. A further change of pH from 7 to 10 should accordingly produce no further change in the nature of the absorption. This was tested, and the results were as expected except that with quinaldinic acid there was a slight difference in the absorption curves at pH 7 and 10. However, this is easily explicable in view of the presence of the carboxyl group and its possible ionization as well as a certain amount of zwitterion formation. Thus the results confirm the attribution of the spectral differences to the presence of different molecules and conversely enable the latter to be identified from the spectra.

2. The differences in spectra at pH's 4 and 7 are of two sorts : (a) a change in ν_1, the wave-number of the first maximum, i.e. the maximum corresponding to the least possible energy difference in a transition between lower and upper states of the absorbing molecule, and in which a minimum of the absorbed energy is used to excite higher vibrational levels in the upper state ; and (b) a change in the intensity of absorption measured by ε, and in particular a change in ε_1, the value at ν_1.

TABLE 1.

Substance.	Solvent.	ν_1.	ε_1.	ν_2.	ε_2.	ν_3.	ε_3.
Pyridine(1)	pH 4.	39,150	5,200	>40,500	—	—	—
,, ...	pH 7.	39,200	2,650	39,840	2,400	>40,500	—
,, ...	Iso-octane(2).	39,100	1,660	39,600	1,760	—	.. —
Quinoline(1) ..	pH 4.	32,050	5,850	—	—	—	—
,, ..	pH 7.	32,050	2,950	33,300	3,100	35,700	3,280
,, ..	Hexane(3).	32,100	6,310	—	—	—	—
Iso-quinoline(1) ..	pH 4.	30,200	4,200	37,040	2,220	>40,500	—
,, ..	pH 7.	31,450	2,560	32,570	2,220	37,750	3,080
,, ..	Hexane(3).	31,700	3,160	—	—	—	—
Quinaldine(1) ..	pH 4.	31,750	7,300	>40,500	—	—	—
,, ..	pH 7.	33,170	3,600	36,100	3,500	—	—
Quinaldinic acid(1)	pH 4.	31,250	6,550	>40,500	—	—	—
,, ,,	pH 7.	34,400	4,250	>40,500	—	—	—
2-picoline(1) ..	pH 4.	38,050	7,200	38,300	7,200	—	—
,, ...	pH 7.	38,250	4,860	—	—	—	—

(1) At pH 4 will be in the form of the ion.

(2) American Petroleum Institute Research Project 44, National Bureau of Standards Catalog of Ultraviolet Spectrograms, Serial No. 108.

(3) International Critical Tables, V (1929).

3. Changes in v_1 did not occur in the cases of pyridine, 2-picoline and quinoline but did occur in every other case as a shift towards the red with change of pH from 7 to 4. The magnitude of the shift varied, although that in quinaldine was equal to that in iso-quinoline. It is unlikely that the quinaldinic acid shift which is far greater than either of the latter two is comparable because of the obliteration of all the partial band structure in the quinaldinic acid spectrum at pH 7 and consequent measurement of v_1, at a higher value than that corresponding to a transition to the lowest possible vibrational level of the upper state. The increasing blurring of structure is consistent with introduction of progressively more massive groups into the quinoline nucleus in the order —H, —CH_3, —COOH. No explanation can be advanced at present for the similarity of the shift in the cases of quinaldine and iso-quinoline.

The similarity of v_1 for pyridine (2-picoline, quinoline) and its ion means that the introduction of a hydrogen nucleus and of a positive charge into the molecule has the same effect on the energy of each level concerned in the transition, thus preserving a constant difference between the two. It does not necessarily mean that the introduction of a positive charge is without any effect on the potential energy of the molecular orbitals ; it would be remarkable if this were so, since it would imply that the field in which the electrons moved was unaffected by the increased nuclear charge.

4. Change in ε_1 was invariably an increase as the pH changed from 7 to 4. The values of R $[=(\varepsilon_1)_{pH\,4} : (\varepsilon_1)_{pH\,7}]$ are given in Table 2.

TABLE 2.

Substance.	R
Pyridine	1·98
2-picoline	1·50
Quinoline	1·98
Iso-quinoline	1·63
Quinaldine	2·03
Quinaldinic acid	(1·70)(1)
Acridine(2)	2·2
Mean	1·9

(1) This figure is not strictly comparable for the reason mentioned above and is omitted from the mean.

(2) Calculated from graphs of Craig and Short (1945).
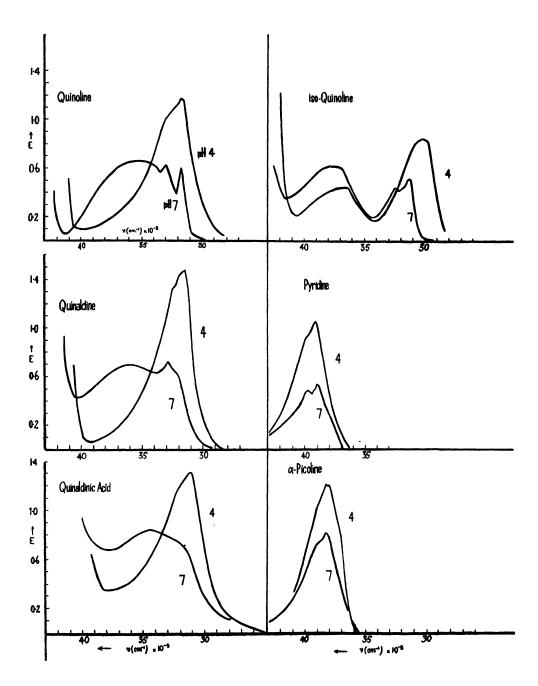
Although a better method of measuring the intensity of absorption is by the area enclosed by the curve, the values obtained for R show clearly the general trend and the closeness of the values for pyridine, quinoline and quinaldine is especially interesting, as is the similarity of the absolute value of ε_1 for pyridine and quinoline, indicating that the fusion of a benzene ring with a pyridine ring is without effect upon the intensity of short wave-number absorption despite the shift in the location of the absorption.

5. ε at other wave-numbers was in every case greater over a considerable range at pH 7 than at pH 4. However, the total absorption as measured by the

area $\int_{v=0}^{40,000 \text{ cm.}^{-1}} \varepsilon dv$ was always about 25% greater at pH 4 than at pH 7.

It is hoped to consider the spectra of these molecules from a theoretical point of view at a later date.

6. By noting the pH at which the absorption changes from that of $\equiv NH^+$ to that of $\equiv N$ a method is available for determining the pK value of $\equiv NH^+$ compounds.

SUMMARY.

The ultra-violet absorption spectra of pyridine (I), 2-picoline (II), quinoline (III), quinaldine, quinaldinic acid and iso-quinoline have been measured in buffered aqueous solutions of known pH. In every instance the absorption at pH 4 differed from that at pH 7 in that the intensity of the long wave-length band was increased by a factor of approximately two and, except for I, II and III, was shifted from the red. This behaviour is attributed to the formation of the ion at pH 4.

The introduction of H^+ into I, II and III affects equally the energies of the two molecular orbitals concerned in a transition, but this is not so with the other three compounds.

The method of ultra-violet absorption spectra is suited to the determination of pK values for pyridine type compounds.

REFERENCES.

Craig, D. P., and Short, L., 1945. *J. chem. Soc.*, 419.
Loofbourow, J. R., and Stimson, M. M., 1940. *Ibid.*, 844 and 1275.
Turnbull, 1945. *Ibid.*, 441.

NITROGEN IN OIL SHALE AND SHALE OIL.

X. NITRILES IN SHALE OIL.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

INTRODUCTION.

The only nitrogen compounds that have yet been isolated and identified from shale oil are pyridine homologues, though pyrroles have also been identified as a class (Mapstone, 1948a). Apart from these, and the presence of possible traces of primary amines (Mapstone, 1948a), no other classes of nitrogen compounds appear to have been detected in crude shale oils. This is probably due to the difficulty of isolating and examining the weakly basic and non-basic nitrogen compounds from the oil, even though less than 20% of the nitrogen present in crude shale oil is sufficiently basic to be extracted by dilute acids. It is of interest that more than 20% of the nitrogen is not extracted even by concentrated sulphuric acid (Mapstone, 1948e).

A review of the pyrolytic reactions that may be involved in the carbonisation of oil shale to produce crude shale oil, suggested that nitriles may be present in the oil in small amounts (Mapstone, 1948c, 1948d). The work described in this paper was carried out in an attempt to detect nitriles as a class in crude shale oil.

HYDROLYSABLE NITROGEN IN CRUDE SHALE OIL.

Previously, it had been found that the distillation of the oil with caustic soda solution required several hours before all the ammonia was distilled (Mapstone, 1945). This prolonged treatment would cause hydrolysis of any amides or nitriles, and the total ammonia evolved would be that from these sources, as well as that from free ammonia and ammonium salts initially present in the oil. At the same time, some of the lower boiling pyridine homologues present could be expected to distil along with the small amount of oil which came over with the ammonia and steam, and these would be recorded as ammonia. The original method was therefore modified, and the different factors examined in turn.

The proportion of oil distilling with the steam was reduced appreciably by using a fractionating column. In this respect a twelve pear column, although slightly more efficient that a four pear column, increased the time required for the distillation between two- and three-fold. By using a low heating rate, the fractionating column acted as a reflux condenser. Handling losses, etc., were greatly reduced by gently refluxing the oil with the caustic soda solution for a while, and then distilling off the ammonia with a fair amount of steam at a faster rate.

In the absence of an antifoaming agent, it was almost impossible to carry out a test. Cresylic acid was a very effective antifoaming agent, and better than amyl or butyl alcohols, which, though effective at the start, passed over with the steam during the distillation, so that serious foaming was sometimes experienced near the end of the test.

Between 50% and 60% of the tar bases present in the oil which distilled with the ammonia and water were extracted by the boric acid and titrated as ammonia. The oil distillate recovered from a series of tests using unwashed crude shale oil contained approximately 0·045% by weight of basic nitrogen.

Once the principle of the analytical method was established, a series of analyses was carried out, using the same sample of crude oil. The results obtained decreased steadily throughout the series from about 130 to 60 p.p.m. by weight of nitrogen in the oil. This decrease was shown to be most probably due to loss of free ammonia by the reduction of the hydrolysable nitrogen content of a fresh sample of oil from 132 to 55 p.p.m. by bubbling with air overnight.

EFFECT OF ACID WASHING ON HYDROLYSABLE NITROGEN.

Preliminary experiments indicated that, even in the absence of ammonia, the hydrolysable nitrogen content of the crude shale oil was reduced by washing the oil with dilute acids (Table I). A further series of experiments was therefore carried out by acid washing solutions of various nitriles and of oleamide in acetic acid-washed crude shale oil.

TABLE I.
Acid Washing Crude Shale Oil.

Acid.	Amount of Acid.	Washing Time.	Water Wash.	Hydrolysable Nitrogen. (Parts per Million.)
Nil	—	—	—	90
Acetic 5%	400 ml./l.	½ hour.	Nil.	56
Acetic 5%	400 ml./l.	½ hour.	500 ml./l.	72
Acetic 5%	400 ml./l.	16 hours.	Nil.	60
Acetic 5% twice	400 ml./l.	¾ hour.	500 ml./l.	47
Acetic 25%	150 ml./l.	½ hour.	500 ml./l.	37
Acetic 25% twice	150 ml./l.	¾ hour.	500 ml./l.	28
Acetic 25%	150 ml./l.	17 days.	500 ml./l.	26
Acetic glac.	10 ml./l.	½ hour.	2 × 500 ml./l.	56
Acetic glac. twice	10 ml./l.	¾ hour.	2 × 500 ml./l.	53
Acetic glac.	10 ml./l.	16 hours.	2 × 500 ml./l.	53
Sulphuric 5%	400 ml./l.	1 hour.	Nil.	34
Sulphuric 5%	400 ml./l.	1 hour.	500 ml./l.	38
Sulphuric 5%	400 ml./l.	16 hours.	500 ml./l.	28
Sulphuric 10%	170 ml./l.	1 hour.	500 ml./l.	34
Sulphuric conc.	40 ml./l.	1 hour.	3 × 500 ml./l.	35

The results obtained (Table II) indicated that the most of any acetonitrile present was removed by the washing. As the molecular weight of the nitriles increased, the proportion extracted by the dilute acids generally decreased, although benzyl cyanide was the least extractable of the nitriles examined. Oleamide was several times as readily extracted as cetyl cyanide, a difference which appears due to the difference in the properties of the polar groupings rather than in the hydrocarbon chains.

By washing with 5% sulphuric acid and separating immediately, and then washing another portion of the sample and leaving it in contact with the acid overnight, it was hoped that some measure of the amount of hydrolysis occurring during the washing could be obtained. The results (Table II) suggested that there was little, if any, hydrolysis at the oil-acid interface.

I I

TABLE II.

Effect of Acid Washing on Nitriles in Crude Shale Oil.

Organic Cyanide Added.	Nil. p.p.m. N.	Acid Treatment.					
		250 ml./l. of 5% H$_2$SO$_4$ then H$_2$O.		250 ml./l. 5% H$_2$SO$_4$ overnight then H$_2$O.		50 ml./l. glac. HAc then 2 × 500 ml./l. of H$_2$O.	
		p.p.m. N.	% Loss.	p.p.m. N.	% Loss.	p.p.m. N.	% Loss.
Unwashed oil	97	—	—	—	—	—	—
Washed oil	31	26	16	19	39	—	—
Benzyl	564	520	6	557	1	570	1
Methyl	1300	271	79	170	87	43	97
Butyl	248	145	42	180	27	138	44
Cetyl	41	34	17	31	24	37	10
Cetyl	94	81	14	78	17	85	10
Oleyl amide	776	188	76	216	72	253	67

MILD REDUCTION OF CRUDE SHALE OIL.

If the hydrolysable nitrogen compounds in the crude shale oil were nitriles, reduction of the oil should decrease or even eliminate them. Because it was neutral and would therefore not hydrolyse the nitriles during the reduction, aluminium amalgam was chosen as the reducing agent.

As a preliminary test, four litres of acetic acid washed crude shale oil were refluxed for eight hours with 121 grammes of amalgamated aluminium strip. The hydrolysable nitrogen contents of the washed oil, the reduced oil, and the reduced oil plus 1·6 ml./l. of aceto nitrile were determined, together with the effect of a mild acid wash. The results (Table III) indicate a significant reduction of the hydrolysable nitrogen content of the oil, and that the remaining compounds were more readily extracted with acid.

TABLE III.

Effect of Reduction of Oil by Aluminium Amalgam.

Oil Treatment.	Nil. p.p.m. N.	Acid Treatment.					
		250 ml./l. 5% H$_2$SO$_4$ then H$_2$O wash.		250 ml./l. 5% H$_2$SO$_4$ overnight then H$_2$O wash.		50 ml./l. glac. Hac. then 2 × 500 ml. H$_2$O.	
		p.p.m. N.	% Loss.	p.p.m. N.	% Loss.	p.p.m. N.	% Loss.
Washed crude oil ..	47	31	34	38	19	40	15
Washed crude oil refluxed over Al-Hg ..	29	16	45	12	59	18	38
Reduced crude oil plus some aceto nitrile ..	521	367	29	238	54	149	71

A further experiment was carried out in which a slow stream of air was passed through four litres of unwashed crude shale oil refluxing over aluminium

amalgam, and then through a solution of boric acid. Samples of the oil were withdrawn each four hours, and the hydrolysable nitrogen content determined. No ammonia was evolved during the progress of the reduction. After one sample of crude oil had been refluxed with the aluminium amalgam for 24 hours, some benzyl cyanide was added (5 ml. to 3·2 l.) and the refluxing continued. The results obtained (Table IV) showed that the hydrolysable nitrogen content of the oil was reduced appreciably by the treatment, and that the rate of reduction decreased with time. This is consistent either with decreasing activity of the amalgam or with the initial more rapid reduction of some of the more reactive hydrolysable nitrogenous compounds. The results after the addition of the benzyl cyanide were inconclusive.

TABLE IV.

Reduction of Hydrolysable Nitrogen by Aluminium Amalgam.
Results in p.p.m. of Hydrolysable Nitrogen.

Oil Sample.	Time Refluxed with Aluminium Amalgam.					
	Nil.	4 Hours.	8 Hours.	12 Hours.	16 Hours.	24 Hours.
(i) Unwashed crude oil	104	67	40	—	—	—
(ii) Unwashed crude oil	47	37	35	34	—	33
(iii) Crude oil from (ii) plus some added benzyl cyanide ..	101	99	98	—	96	—

The reduction of the nitriles should give rise to primary amines, and the detection of these in increased amounts in the crude shale oil after reduction with the aluminium amalgam would confirm the presence of nitriles in the oil. The 10 to 40 p.p.m. reduction in the hydrolysable nitrogen content of the oil obtained should be a measure of the amount of primary amine produced. This was far too small an amount of amines to be determined quantitatively, as the basic nitrogen content of the oil is of the order of one thousand times as much.

McKee claimed to have detected traces of primary amines in shale oil with nitrous acid (Mapstone, 1948a; McKee, 1925) and Horne, Finley and Hopkins obtained similar results using the carbylamine reaction (Mapstone, 1948a; Horne, Finley and Hopkins, 1938). Since the latter test seemed to be the better of the two, it was applied to samples of the crude shale oil which had been treated in various manners. Because of the very low amount of amine being sought, the samples were submitted to a jury of nine for comment. They were asked to classify the results as positive, possible, or negative, and no one was allowed to know either the history of any sample or any previous verdict until he had given his own decision.

The results of the tests (Table V) indicated a fair divergence in sensitivity of smell of the different " jurymen ", but all knew the odour of carbylamine beforehand, and no one gave all results negative. The only sample on which the opinion was unanimous was that which had been washed with acetic acid, and which would, therefore, contain no basic compounds. The results suggest that refluxing the oil with aluminium amalgam did increase the primary amine content of the oil very slightly from a " possible " trace to a " probable " trace. Weathering the oil had little effect on the primary amine content, but refluxing with solid caustic potash or hydrolysis with caustic soda solution reduced it, which may have been due to the loss of volatile amines during the treatment.

TABLE V.

Results of Carbylamine Test on Various Samples of Crude Shale Oil.
(Summary of nine opinions.)

Shale Oil Sample.	Positive.	Possible.	Negative.
1. Fresh crude oil	2	1	6
2. Fresh crude oil plus 0·1% aniline	8	Nil	1
3. Crude oil weathered 2 years	2	1	6
4. Crude oil refluxed over solid KOH	Nil	2	7
5. Crude oil washed with acetic acid	Nil	Nil	9
6. Crude oil refluxed 6 hours with Al-Hg	2	6	1
7. Crude oil refluxed 18 hours with Al-Hg and then hydrolysed	Nil	1	8
8. Crude oil plus 0·1% benzyl cyanide refluxed 6 hours with Al-Hg	3	1	5
9. Crude oil plus 0·1% benzyl cyanide refluxed 18 hours with Al-Hg and hydrolysed	4	3	2
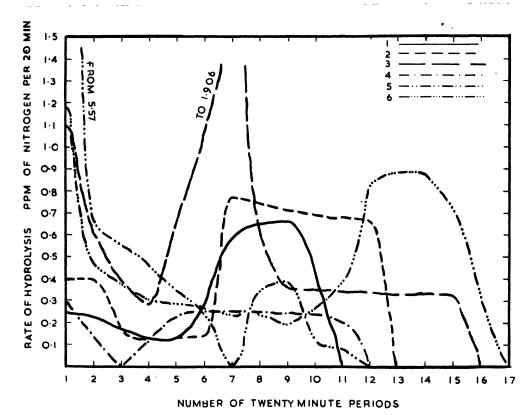
Fig. 1.

Fig. 1.—Rate of Hydrolysis of some Crude Shale Oils.
Sample No. 1. Acetic acid washed oil.
   ,,   No. 2. Acetic acid washed oil plus added benzyl cyanide.
   ,,   No. 3. Unwashed crude oil.
   ,,   No. 4. Unwashed crude oil after refluxing with Al-Hg for 20 hours.
   ,,   No. 5. Unwashed crude oil.
   ,,   No. 6. Weathered crude oil.

The aluminium amalgam reduction of the crude oil containing benzyl cyanide gave a definite increase in the primary amine content, which appeared to increase with time of refluxing.

RATE OF HYDROLYSIS OF CRUDE SHALE OIL.

Both amides and nitriles could exhibit most of the properties of the hydrolysable nitrogen components of the oil. A consideration of their properties suggested that it might be possible to distinguish between them by determining the rate of hydrolysis of the oil and of some amides and nitriles in solution in the oil, despite the small amount present.
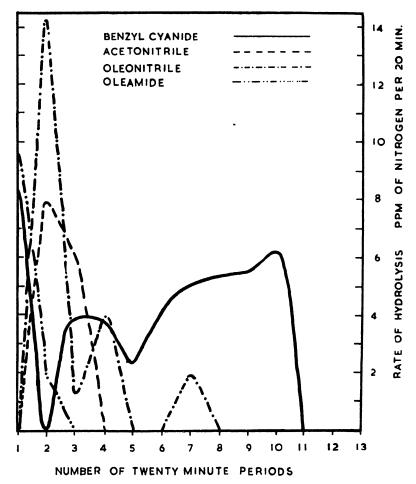
Fig. 2.

The results obtained with various samples of crude shale oil are presented graphically in Figure 1. With the samples of acid washed oil, the rate of ammonia evolution was not very high at first, and soon fell to a minimum which was followed by a pronounced peak or plateau in the rate curve. With the samples that had not been acid washed, the initial rate of ammonia evolution was much higher, but the peak or plateau was still observed in the latter part of the rate curve. This initially higher rate could be attributed to a combination of three factors : the possible presence of ammonium salts and the presence of

volatile tar bases in the crude shale oil together with the decomposition of some of the more readily hydrolysable compounds. All or part of these materials would be removed by the acid wash.

The results of the rate of hydrolysis of oleamide and some nitriles are presented graphically in Figure 2. The hydrolysis rate curves for the nitriles were of the same general type as those of the acid washed crude shale oil, by giving a pronounced minimum followed by a peak or plateau. Oleamide gave a rapidly decreasing rate curve without any indication of a subsequent peak.

Another inference drawn from this work was that the duration of the hydrolysis was a function of the amount of hydrolysable material present. This may be expected, as the rate of hydrolysis would be a function of the degree of contact between the oil and the caustic solution. Also, the rate of hydrolysis is obviously a function of the structure of the nitrile.

The significant difference in the hydrolysis rate curves for oleamide and for the nitriles suggests that the occurrence of a peak or plateau in the curve may be used as a tentative indication of the presence of nitriles in the oil. At present, no explanation can be given for the shape of the hydrolysis rate curve of the nitriles, though it appears that it may be due to the fact that the hydrolysis is a two-stage reaction in first giving rise to the amide. It is quite probable that some amides, as well as nitriles, may be present in the oil, but this method could not very well be employed to detect amides in the presence of nitriles.

FORMATION OF ORGANIC ACIDS ON HYDROLYSIS OF CRUDE SHALE OIL.

The results presented in Table VI show a fairly close correspondence between the amount of ammonia evolved on hydrolysis of the oil and the amount of organic acids formed at the same time. The discrepancies are relatively large, ranging from 20% to 50% of the amount of ammonia obtained, but the maximum difference was only 5·3 mg. of ammonia from 500 ml. of oil. Also, the necessarily involved method of isolation of the organic acids and the possibility of the presence of traces of esters in the crude oil, could tend to give high results, while any discrepancies in the determination of the ammonia would, if anything, tend to give low results. Since the acid obtained in each case was in excess of the ammonia liberated, the results can be interpreted with a reasonable degree of certainty as supporting the previous deduction that the hydrolysable nitrogen compounds present in crude shale oil are nitriles, and possibly some amides.

TABLE VI.

Organic Acids from the Hydrolysis of Crude Shale Oil.

(Results are expressed in mg. of ammonia as obtained from 500 ml. of acid washed oil.)

Sample No.	Ammonia.	Organic Acids.
A	7·9	13·2
B	10·4	12·3
C	10·7	13·2

SUMMARY.

From an examination of the effect of acid washing and of mild reduction on the hydrolysable nitrogen content of the crude shale oil, the rate of hydrolysis of the oil, and the determination of the amounts of organic acids formed by the hydrolysis of the oil, it appears that the hydrolysable nitrogen compounds

which are present in crude shale oil to the extent of 30-100 p.p.m. of nitrogen by weight are most probably nitriles.   Traces of amides may also be present.

ACKNOWLEDGEMENTS.

EXPERIMENTAL.

Determination of Hydrolysable Nitrogen.

A measured volume (generally 50 or 100 ml.) of crude shale oil and 150 ml. of 10% caustic soda solution was charged into a long-necked flask of 500 to 750 ml. capacity, and 5 ml. of commercial cresylic acid or amyl or butyl alcohol added.   The flask was then fitted with a four pear fractionating column fitted to a condenser, the delivery from which dipped below the surface of 50 ml. of 2% boric acid in a dropping funnel.   The funnel was sealed and fitted with a bunsen valve (Meneghini, 1945) to reduce the danger of an accidental " suck back ".   Heating was commenced, and maintained at a sufficiently low rate for the liquid to boil in the flask, but for very little to distil, the fractionating column acting as a dephlegmater at almost total reflux. After an hour the rate of heating was increased, so that approximately 100 ml. of water were distilled during the next half hour.   After the distillation had been completed, the lower aqueous layer of the distillate was separated, and the oil distillate washed with 25 ml. of ammonia-free distilled water.   This was added to the separated boric acid solution, which was then titrated with 0·05 N sulphuric acid, using screened methyl orange as indicator (I.P., 1946).   This separation step was necessary, as otherwise the oil interfered with the titration by extracting the methyl orange from the aqueous phase.

Washing Crude Shale Oil with Glacial Acetic Acid.

In order to extract free ammonia and the tar bases from a sample of crude shale oil before using it for other work, it was necessary to acid wash it.   The washing was carried out by mixing thoroughly the required amounts of oil and glacial acetic acid (which was soluble in the oil), and adding the required amount of water.   The dilute acid layer was then separated, and the oil washed with a further amount of water.

Carbylamine Test on Crude Oil.

This test was carried out by boiling 10 ml. of the crude shale oil with 0·5 ml. of chloroform and 1·0 ml. of 10% caustic soda solution.   All samples were prepared and, when cool, were submitted together to the " jury " for smelling.

Determination of the Rate of Hydrolysis of Crude Shale Oil.
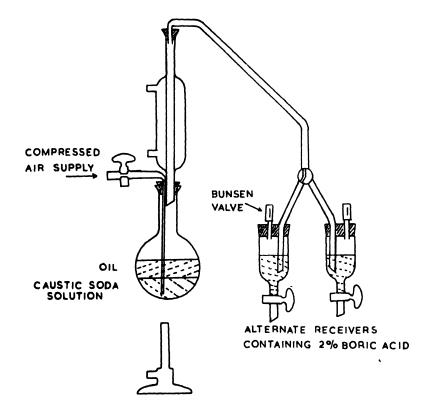
Crude shale oil (250 ml.), 10% caustic soda solution (300 ml.), and cresylic acid (10 ml.) were charged into a 750 ml. bolthead flask fitted up as in Figure 3.   The air flow was controlled so that three bubbles per second escaped through the boric acid solution in the receiver, and heating was commenced.   The current of air served the dual purpose of carrying off the ammonia as it was liberated, and of mixing the oil and the caustic soda solution and eliminating bumping during the boiling.   Zero time for the hydrolysis was taken as the time the mixture started to boil, as shown by the return of liquid condensate from the condenser.   From that time, the air stream was diverted to alternate receivers containing boric acid, at 20 minute intervals.   After the air had been diverted from a receiver, the aqueous layer was carefully separated from any oil that had distilled, and titrated with 0·05 N sulphuric acid, using screened methyl orange as the indicator.   This process was repeated until at least three consecutive titrations indicated that no ammonia had been evolved during the period.   The experiments were carried out in duplicate and the results averaged.

The rates of hydrolysis of the oleamide and the nitriles were determined by adding some of the compound to 250 ml. of the oil which had been completely hydrolysed.   Equal amounts were added to each of two samples of oil, and the rates of hydrolysis of the two samples averaged.

Formation of Organic Acids on Hydrolysis of Crude Shale Oil.

A quantity of the crude shale oil to be tested was acid washed to remove ammonium salts and volatile tar bases, which could interfere with the analysis, and then washed several times with hot water to remove any residual traces of acid. The final washings were neutral to alkali blue.

Five hundred ml. of the washed oil were refluxed with 100 ml. of 10% caustic soda solution and 5 ml. of cresylic acid, in the same apparatus as used for the determination of the rate of hydrolysis, so that it was possible to determine when the hydrolysis was complete, as well as the total amount of ammonia evolved. The lower caustic soda layer was indistinguishable from the oil layer, except in bright sunlight or ultra-violet light, when the oil fluoresced a strong green.

COMPRESSED
AIR SUPPLY

BUNSEN VALVE

OIL
CAUSTIC SODA SOLUTION

ALTERNATE RECEIVERS
CONTAINING 2% BORIC ACID

APPARATUS FOR DETERMINATION OF RATE OF HYDROLYSIS OF OIL

Fig. 3.

The two layers were separated, and the oil washed with two 50 ml. portions of hot water. The combined caustic extract and washes were acidified with concentrated hydrochloric acid, and extracted with 100 ml. of gasoline. The gasoline was washed twice with 100 ml. portions of distilled water before the total (organic) acidity was determined by I.P. Method 1/46 (I.P. 1/46, 1948).

Before hydrolysis, the organic acid content of the crude oil was nil. A blank test indicated that the 5 ml. of cresylic acid added to act as an antifoaming agent during the hydrolysis contained organic acids equivalent to 0·73 mg. of ammonia. This was allowed for in calculating the amount of organic acids formed by the hydrolysis of the oil.

REFERENCES.

Horne, J. W., Finley, W. F., and Hopkins, C. P., 1938.   *U.S. Bur. Mines Bull.*, No. 415, Chap. 9, compiled by B. Guthrie.

I.P. 1/46, 1948.   Standard Methods for Testing Petroleum and its Products.   Institute of Petroleum, London, 9th Ed.

Mapstone, G. E., 1948*a*.   THIS JOURNAL, **82**, 85-90.

———————— 1948*b*.   *Ibid.*, **82**, 91–95.

———————— 1948*c*.   *Ibid.*, **82**, 96–106.

———————— 1948*d*.   *Ibid.*, **82**, 129-134.

———————— 1948*e*.   *Ibid.*, **82**, 135–144.

———————— 1945.   *Petroleum Refiner*, **24**, 219.

McKee, R. H., 1925.   Shale Oil.   *A.C.S. Monograph No. 25.*   Chemical Catalogue Publishing Co., New York.

Meneghini, M., 1945.   *Ind. Eng. Chem. Anal. Ed.*, **17**, 672.

SYNTHETIC SEX HORMONES.

PART II. THE PINACOLS AND PINACOLONE OF p-METHYLMERCAPTOPROPIO-PHENONE, AND THE PREPARATION OF DITHIODIENESTROL DIMETHYL ESTER.

By G. K. HUGHES, B.Sc.

and E. O. P. THOMPSON.

The successful dehydration of the pinacols from p-hydroxyacetophenone by Dodds, Goldberg, Lawson and Robinson (1939) to the corresponding butadiene, suggested the possibility of dehydrating the *pinacols*, II, derived from p-methylmercaptopropiophenone, I, to the sulphur analogue of dienestrol dimethyl ether IV. With potassium bisulphate or acetyl chloride, only the

pinacolone III was isolated. However, both the *meso* and *dl* forms of the pinacol gave with a mixture of acetic anhydride and acetyl chloride (cf. Dodds *et al.*, 1939), along with the pinacolone, a white crystalline solid which is the *hexadiene* IV.

Several methods of preparing the pinacols, II, were studied. Electrolytic reduction of the ketone, in an aqueous alcoholic solution containing potassium acetate, with a lead cathode as described by Price and Mueller (1944) gave a mixture of the pinacols which were separated readily owing to their different solubilities.

The high melting isomer is moderately soluble in hot benzene or alcohol and almost insoluble in ether, whereas the low melting pinacol is readily soluble in most organic solvents and can only be crystallized with difficulty from petroleum ether.

The method of Bachmann (1933) using sodium amalgam with alcohol in ether-benzene solution gave a good yield of the pinacols. With diaryl ketones this method gives a quantitative yield of the corresponding hydrol, the highly coloured sodium ketyl radicals being formed as intermediates. Possibly the reduction of p-methylmercaptopropiophenone proceeds by a different mechanism as no marked colour was developed. Magnesium and magnesium iodide which Gomberg and Bachmann (1927) introduced for the preparation of pinacols from diaryl ketones in quantitative yield (coloured iodomagnesium ketyl radicals being formed in the reaction) gave only small yields (8%) of the high melting pinacol, an olive green colour accompanying the reaction. However, Bachmann and Ferguson (1934) reported poor yields of pinacols from diaryl ketones containing alkoxyl groups with this reagent.

Aluminium amalgam and alcohol as used by Newman (1940) gave a fair yield of the pinacols.

Zinc dust and acetic acid used by Bachmann and Ferguson (1934) for the preparation of pinacols from diaryl ketones gave no detectable amounts of the pinacols but some thioanethole, V, was formed due to the easy dehydration of the hydrol as described by Hughes and Thompson (1948).

The pinacols were identified by oxidation with lead tetra-acetate as used by Price and Mueller (1944). The low melting pinacol was rapidly oxidized to the ketone, I, which was isolated quantitatively as the phenylhydrazone. The high melting isomer was oxidized slowly and using excess lead tetra-acetate the sulphoxide of p-methyl mercaptopropiophenone was isolated as its phenyl-hydrazone.

Attempts to identify the ketone, I, by selective oxidation with selenium dioxide followed by periodic acid, to p-methylmercaptobenzoic acid gave instead the sulphoxide of this acid. Mel'nikov (1935) had previously reported the oxidation of sulphides to sulphoxides and sulphones by selenium dioxide.

Attempts to esterify the high melting pinacol with acetic anhydride and pyridine, and by the Schotten Baumann method with benzoyl chloride, were unsuccessful, the pinacol being recovered unchanged.

Both pinacols were readily rearranged with acetic anhydride and sulphuric acid (Price and Mueller, 1944) and iodine and acetic acid (Gomberg and Bachmann, 1927); the latter method gave the better yield.

The pinacolone obtained would not give a dinitrophenylhydrazone or an oxime using the most stringent conditions of Bachmann and Barton (1938). This agrees with the observation of Sisido and Nozaki (1948) on the oxygen analogue.

Price and Mueller (1944) using the somewhat similar pinacolone 2 : 2'-di-(p-methoxyphenyl)-butan-3-one VI did obtain an oxime. Heating the pinacolone III, with hydroxylamine hydrochloride and alcohol in a sealed tube for six hours at 160° C. gave no oxime or rearranged product the pinacolone being recovered unchanged. Under similar conditions, Feith and Davies (1891) obtained N-acetyl-mesidine from acetomesitylene which under normal conditions will not form an oxime.

The structure of the pinacolone was assumed to be III, by analogy with the pinacolone obtained by Wessely, Kerschbaum, Kleedorfer, Prillinger and Zajic (1940). It gave a positive test for an enolizable hydrogen atom with *m*-dinitro-benzene and alkali in pyridine solution.

A 25% methyl alcohol solution of caustic potash did not split the pinacolone after eighty hours' refluxing.

This structure was confirmed by oxidation of the pinacolone or its sulphone with chromic acid to $p : p'$-dimethylsulphonylbenzophenone.

EXPERIMENTAL.

For the preparation of *p*-methylmercaptopropiophenone, see Hughes and Thompson (1948).

Electrolytic Reduction.

The apparatus consisted of a porous pot (fitted with a condenser) which contained the catholyte immersed in a 40% aqueous solution of potassium carbonate. The cathode was made of lead foil 100 sq. cm. in area, and the catholyte was a solution of *p*-methylmercaptopropio-phenone (55 g.) in alcohol (125 ml.) to which water (50 ml.) containing potassium acetate (28 ml. saturated solution) was added. The electrolysis was carried out at reflux temperature using a current density of 0·02 amp./sq. cm., and after passing 120% theoretical current the mixture was poured into water.

The crude material was dissolved in hot alcohol, and on cooling the high melting pinacol separated and was completely removed by concentration of the mother liquors.

The crude high melting pinacol (10 g.) on repeated recrystallization from ethyl alcohol gave white crystals (8 g.) m.p. 168° C.

Found : C, 65·76 ; H, 7·19%. Calculated for $C_{20}H_{26}O_2S_2$: C, 66·23 ; H, 7·23%.

After removal of the alcohol from the mother liquors the residue was repeatedly recrystal-lized from petroleum ether (60–80°) to give the other pinacol m.p. 93° C.

Found : C, 66·00 ; H, 7·31. Calculated for $C_{20}H_{26}O_2S_2$: C, 66·23 ; H, 7·23%.

Reduction with Sodium Amalgam.

To the ketone (10 g.) dissolved in a mixture of anhydrous ether (70 ml.), benzene (70 ml.) and alcohol (7 ml.) was added sodium amalgam (167 g., 2%) and the mixture shaken in a tightly stoppered bottle for two hours.

No marked change in the initial yellow colour was noticed, and the solution gradually became cloudy as the high melting pinacol separated out.

The mixture was poured into water, acidified, and after separation of the organic layer extracted three times with hot benzene. The combined organic extracts were washed with water and the solvents removed under reduced pressure. The residue was mixed with ether and the insoluble pinacol (3·1 g.) filtered off. Evaporation of the ether followed by recrystallization from petroleum ether (60–80°) gave the other pinacol, m.p. 93° (3·9 g.).

The crude mixture of pinacols after removal of solvents may be rearranged with acetic acid and iodine to give the pinacolone (6 g.).

On the basis of yields obtained with pure pinacols this indicates at least 75% yield of pinacols.

Distillation of the crude pinacols under high vacuum gave no pinacol but a mixture of thioanethole V, ketone I and pinacolone III.

The pinacolone probably results from the effect of traces of acid and the ketone and thio-anethole from disproportionation of the pinacols into ketone and hydrol, the latter being readily dehydrated.

Reduction with Aluminium Amalgam.

The ketone (30 g.) in absolute alcohol (300 ml.) and benzene (200 ml.) was treated with aluminium amalgam, prepared from previously etched foil (12 g.) and mercuric chloride (0·5 g.) and the mixture refluxed twenty-four hours. When poured into water and worked up in the manner described for the sodium amalgam method, the pinacols, m.p. 167° (10 g. crude) and m.p. 93° (8 g. crude) were obtained.

Reduction with Magnesium and Magnesium Iodide.

Magnesium iodide prepared by refluxing excess magnesium turnings (2·5 g.), iodine (7 g.) in a mixture of ether (18 ml.) and benzene (25 ml.) was shaken with the ketone (9 g.) in benzene (8 ml.). An olive green colour developed and after shaking three hours the liquid was decanted into water, acidified with hydrochloric acid and extracted with benzene. The organic extracts were washed with water and the solvents removed under diminished pressure. Ether was added to the oil and allowed to stand overnight, when a small amount of high melting pinacol (0·8 g.) separated. No pinacol could be obtained from the ether solution which consisted of unchanged ketone. Rearrangement of the residue after removal of the high melting pinacol gave oils from which no pinacolone could be crystallized.

Reduction with Zinc and Acetic Acid.

The ketone (10 g.) in glacial acetic acid (100 ml.) was treated with zinc dust (20 g.) during the course of two weeks of standing at room temperature. When the solution was decanted into water a semi-solid mixture was obtained which when filtered gave a solid, and an oil with a strong aniseed odour.

The solid was unchanged ketone identified by mixed melting point. The oil was distilled under reduced pressure to give thioanethole (2 g.) b.p. 143° at 25 mm. (approx.) and *p*-methylmercaptopropiophenone, b.p. 190° at 25 mm. (approx.).

Oxidation of the Pinacols with Lead Tetraacetate.

The low melting pinacol (1 g.) was suspended in glacial acetic acid (5 ml.) and the theoretical amount of lead tetraacetate (1·25 g.) was added. When both reactants had dissolved, the ketone was separated as the phenylhydrazone by addition of phenylhydrazine (1 ml.) in glacial acetic acid (3 ml.) and shaking thoroughly with the slow addition of water (2 ml.).

The phenylhydrazone after washing was recrystallized several times from alcohol, m.p. 84°. A mixed melting point with an authentic specimen prepared from *p*-methylmercaptopropiophenone showed no depression.

The derivative decomposed after several hours, and therefore was not analysed.

The high melting pinacol when treated in this way gave no phenylhydrazone unless excess lead tetra-acetate (2·5 g.) was used when a yellow compound was obtained m.p. 175° after several recrystallizations. It did not depress the melting point of an authentic specimen of the phenylhydrazone of the sulphoxide of the ketone.

The phenylhydrazones of the sulphoxide (m.p. 176°) and sulphone (m.p. 150°) of *p*-methylmercaptopropiophenone were prepared in the usual manner from the sulphoxide and sulphone and were recrystallized from alcohol.

Oxidation of p-Methylmercaptopropiophenone with Selenium Dioxide and Periodic Acid.

The ketone (10 g.), selenium dioxide (12·5 g.) and dioxane (60 ml.) were refluxed four hours during which black selenium separated. The solution was decanted and the excess dioxane removed under reduced pressure. The residue was extracted with ether, the ether removed, water (50 ml.), potassium periodate (12·8 g.) and concentrated sulphuric acid (1·5 ml.) added and the mixture shaken and stood overnight. The solid material was filtered off, treated with caustic soda and filtered. The filtrate was acidified and the residue recrystallized from water to give a pale yellow solid (2·2 g.) m.p. 229°, which did not depress the melting point of an authentic specimen of *p*-carboxyphenyl methyl sulphoxide.

The sulphoxide m.pt. 233° and sulphone m.pt. 267° of *p*-methylmercaptobenzoic acid were prepared from the acid by oxidation in the usual way, in acetone and acetic acid solution respectively, with hydrogen peroxide (30%). They both recrystallized from water in white crystals.

Found : C, 51·17 ; H, 4·50 ; S, 17·25%. Calculated for $C_8H_8O_3S$: C, 52·12 : H, 4·38 ; S, 17·4%.

Found : C, 47·26 ; H, 3·94 ; S, 15·75%. Calculated for $C_8H_8O_4S$: C, 47·96 ; H, 4·03 ; S, 16·02%.

Pinacolone Rearrangement.

The pinacol (10 g.) was suspended in acetic anhydride (50 ml.) and concentrated sulphuric acid (1·25 ml.) added drop by drop. A purple colour was obtained which faded to a light brown and all the solid dissolved. The solution was poured into water and neutralized with sodium carbonate when the oil obtained gradually solidified.

The solid was recrystallized from alcohol to give 2 : 2-di-(*p*-methylmercaptophenyl)-hexane-3-one m.p. 90–95°.

Concentration of the mother liquors gave a small amount (0·2 g.) of white solid m.p. 150°. Further concentration gave more pinacolone VI. The pinacolone fractions on repeated recrystallization from alcohol had m.p. 95° C.

Found : C, 69·4 ; H, 6·90%. Calculated for $C_{20}H_{24}OS_2$: C, 69·69 ; H, 7·02%.

The small amount of impurity on recrystallization had m.p. 157°.

Found : C, 65·3 ; H, 6·8%. This was possibly the isomeric pinacolone.

The yield was slightly better, 70%, with the high melting pinacol, the other isomer giving 60% yield.

Alternatively the pinacol (5 g.) was refluxed with acetic acid (25 ml.) and a crystal of iodine for several hours and then poured into water and neutralized. When recrystallized both pinacols gave the pinacolone (3·8 g.) m.p. 95° C. No other product was isolated in this case.

Oxidation of the Pinacolone.

Potassium Permanganate. Formation of the Sulphone. The pinacolone (1 g.) in glacial acetic acid solution was treated slowly with a solution of potassium permanganate (1·37 g.) in water (40 ml.). After addition was complete the solution was decolorized by sulphur dioxide. A white precipitate remained which when recrystallized from methanol gave the sulphone (0·68 g.) m.p. 149·5° C.

Found : C, 57·8 ; H, 6·05 ; S, 15·36%. Calculated for $C_{20}H_{24}O_5S_2$: C, 58·8 ; H, 5·92 ; S, 15·7%.

The sulphone was also obtained by oxidation with hydrogen peroxide solution (30%) in acetic acid solution at 100° C.

Chromic Acid. The pinacolone (1·15 g.) or sulphone (2 g.) was dissolved in glacial acetic acid and chromic acid crystals (2 g.) together with concentrated sulphuric acid (1·3 ml.) added and the mixture refluxed for thirty minutes. The reaction mixture was poured into water and almost neutralized with sodium carbonate. A solid separated which was filtered off, washed with water and recrystallized from water, m.p. 236–237° C.

The compound was *p* : *p-dimethylsulphonyl-benzophenone.*

Found : C, 53·0 ; H, 4·23 ; S, 18·56%. Calculated for $C_{15}H_{14}O_5S_2$: C, 53·2 ; H, 4·17 ; S, 19·0%.

Dithiodienestrol Dimethyl Ether. The pinacol (5 g.) was refluxed with acetyl chloride (6 ml.) and acetic anhydride (9 ml.) for thirty minutes and poured on to ice. The semi-solid material recrystallized from alcohol to give a mixture of pinacolone and diene (3 g.) m.p. 80° C. When taken up in alcohol and cooled slowly the hexadiene (0·7 g.) m.p. 125–133° crystallized out and was carefully filtered off, the pinacolone (2 g.) m.p. 85–93° crystallizing in the receiver.

Repeated recrystallization of both fractions gave the pinacolone (1·3 g.) m.p. 95° C., and the dithiodienestrol dimethyl ether (0·4 g.) m.p. 141°.

Found : C, 72·8 ; H, 6·87 ; S, 19·76%. Calculated for $C_{20}H_{22}S_2$: C, 73·6 ; H, 6·75 ; S, 19·6%.

REFERENCES.

Bachmann, W. E., 1933. *J. Amer. Chem. Soc.*, **55**, 770.
Bachmann, W. E., and Barton, Sister M. X., 1938. *J. Org. Chem.*, **3**, 300.
Bachmann, W. E., and Ferguson, J. N., 1934. *J. Amer. Chem. Soc.*, **56**, 2031.

Dodds, E. C., Goldberg, L., Lawson, W., and Robinson, R., 1939. *Proc. Roy. Soc. (London)*, B, **127**, 140.

Feith, E., and Davies, S. H., 1891. *Ber. dtsch. chem. Ges.*, **24**, 3546.

Gomberg, M., and Bachmann, W. E., 1927. *J. Amer. Chem. Soc.*, **49**, 241.

Hughes, G. K., and Thompson, E. O. P., 1948. THIS JOURNAL, **82**, 262.

Mel'nikov, N. N., 1936. *Uspekhi. Kim.*, **5**, 443 ; *Chem. Abstr.*, **30**, 5180.

Newmann, M. S., 1940. *J. Amer. Chem. Soc.*, **62**, 1683.

Price, C. C., and Mueller, G. P., 1944. *J. Amer. Chem. Soc.*, **66**, 634.

Sisido, K., and Nozaki, H., 1948. *J. Amer. Chem. Soc.*, **70**, 776.

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METALLOGENETIC EPOCHS AND ORE REGIONS IN THE COMMONWEALTH OF AUSTRALIA.*

By W. R. BROWNE, D.Sc.

With one Table and six Text-figures.

CONTENTS.

INTRODUCTION.

The wise old Hebrew prophet well knew the value of the inspiration and encouragement to be got from a contemplation of the illustrious past when he counselled his countrymen : " Look ye unto the rock whence ye are hewn, and the hole of the pit whence ye are digged ; look unto Abraham your father and to Sarah that bare you." It was doubtless with the same thought in mind that the Royal Society of New South Wales ordained that the memory of that great citizen and scientist, Rev. W. B. Clarke, who may be regarded as its second founder, should be kept green by the delivery of an annual lecture dedicated to his name. I am very proud and honoured to have been asked by the Council to be the lecturer for this year, for I have long been an ardent admirer of the " father of Australian geology ", of his geological enthusiasm, scientific insight, tireless energy, single-minded devotion to duty and uncompromising champion-ship of what he was convinced was right. The pioneer geological work that he accomplished in the face of many obstacles must ever be an inspiring influence to geologists in this country.

Like his successors, David and Andrews, in the same field of investigation, Clarke combined an ardent love of geology for its own sake with a strong deter-mination to apply his knowledge for the material advancement of his country. The implied recognition of the twofold character of geology is apt to be obscured alike by those who think of it simply and solely as a means to material gains and by those rare souls whose thoughts never stray from the pursuit of the so-called academic aspects of their studies. Only in so far as it holds a proper

balance between the cultural and the utilitarian can geological science in this country hope to command the respect and attention that it merits and make the progress that it should.

For my lecture to-night I have chosen a theme which, while strictly speaking in the realm of pure geology, yet should hold some interest for the economic geologist, since the study of ore-deposits stands to gain from every attempt to arrange our knowledge in orderly fashion. From time to time there have been papers written and addresses given on the questions of metallogenetic epochs and ore provinces in various parts of the Commonwealth and in the continent as a whole. One thinks particularly of papers by E. S. Simpson and E. C. Andrews, by Waterhouse, Stillwell and Ball, and of the more recent work of E. S. Hills and Austin Edwards and the presidential addresses of Jones in Queensland and Prider in Western Australia.* While deriving much from all this earlier work, my present intention is chiefly to analyse our information about the ore-deposits of Australia in the setting provided by an increased knowledge of the epochs of tectonic and igneous activity. The result must be regarded merely as a progress report and an interpretation, some part of which is bound later to be rejected and some to be modified.

If we were to consider ore-deposits in a very comprehensive way so as to include those of detrital or otherwise derivative character, we could recognise an almost endless succession of ore epochs, which would include the time of deposition of the very important pre-Cambrian sedimentary iron ores of Western Australia and South Australia, the Tertiary periods during which our laterites and bauxites and our alluvial gold and tin deposits were formed, and the Quaternary epochs marked by the concentration of the very valuable zircon and rutile deposits at various places along the coast of eastern Australia and Tasmania. We shall, however, confine our attention to the primary ore-deposits, that is to say, those deposits of ores which are related to the igneous rocks.

GEOGRAPHICAL DISTRIBUTION OF ORE-DEPOSITS.

Australia may be broadly divided into three great topographic regions (Fig. 1) : (a) the Great Western Plateau, including the pre-Cambrian shield and stretching over Western Australia, the greater part of Northern Territory and much of South Australia, with extensions into the far west of Queensland and New South Wales ; (b) the Central-Eastern Lowlands, made up largely of the Mesozoic sediments of the Great Australian Artesian Basin and the Cainozoic deposits of the Murravian Basin ; and (c) the Eastern Highlands belt, composed mainly of Palæozoic rocks and occupying much of eastern Queensland and New South Wales, the greater part of Victoria and virtually all of Tasmania.

The primary ore-deposits are confined to the first and third regions, wherein the rocks have been folded again and again and invaded by igneous magmas, most of which were ore-carriers. The strata of the second region are level-bedded, and their deposition has been unaccompanied by volcanic activity on a large scale. There are also in the plateau regions marginal areas of barren, horizontal or gently folded strata, such as the Desert Basin and the North-West and South-West Basins in Western Australia, the Nullarbor Plain, the areas occupied by Mesozoic rocks in all the States and the great Sandridge Deserts. Some of these form lowlands and some highlands, and on the other hand there are lowlands, particularly in the coastal belts, composed of intensely folded ore-bearing rocks. Nevertheless, broadly speaking, the highland and lowland divisions of Australia have not merely a tectonic and structural but also a considerable economic import.

* See list of references.

The precise conditions of deposition of the Older pre-Cambrian rocks of the Great Western Shield we do not know ; but the Upper pre-Cambrian and Cambrian rocks were laid down in a great median basin of deposition including at least two elongated troughs, one running north and south in South Australia, the other east and west in Central Australia, partly on the site of the Macdonnell Ranges. In the first trough sediments to a maximum thickness of 12 or 15 miles were deposited before it was extinguished by folding of its strata. The Eastern Highlands belt was the site of the great Tasman Geosyncline, wherein sinking and deposition alternated with folding and plutonic injection throughout Palæozoic and Mesozoic time. The geosynclinal strata—chiefly marine—and their associated volcanic rocks became hosts for the metalliferous ores brought in contemporaneously with volcanic activity or introduced with the formation of plutonic bathyliths during the orogenic epochs.

Fig. 1.—Topographic Regions of Australia.
(a) The Great Western Plateau.
(b) The Central-Eastern Lowlands.
(c) The Eastern Highlands Belt.

The blanketing effects of the unfolded post-Palæozoic beds are such that any ore-deposits in the underlying pre-Cambrian and Palæozoic rocks are hidden away as securely as if they did not exist. There is little doubt that ores are present in these old foundation-rocks, but they are at an extreme depth of at least 7000 feet in south-eastern Queensland and more than 5000 feet in the Murravian Basin. There is some reason to believe that the Cretaceous rocks of the Great Artesian Basin once encroached upon the highlands farther than at present, and that the rich ore-deposits of, for instance, Cloncurry in Queensland and Broken Hill and Cobar in New South Wales, have been revealed to us through erosion of the sediments of the Cretaceous epicontinental sea that covered the site of the Great Artesian Basin. Even in known ore-bearing areas a few inches of sand and soil can most effectively conceal the presence of metalliferous rocks,

but nowadays some of the hidden deposits are being detected by geophysical and geochemical prospecting.

RELATION OF ORES TO IGNEOUS ROCKS.

Geologists are not unanimous as to the exact origin and mode of emplacement of ores of the economic metals, but it is a matter of general agreement that they are somehow genetically related to magmas or igneous emanations which ascend from the deeper layers of the earth's crust and come to rest at depth or are ejected on to the surface. The question whether the ore-minerals were original and essential constituents of the magma, or were present in the invaded rocks, ingested by the ascending fluids and later regurgitated, as it were, does not greatly concern us ; neither need we discuss the much debated problem of the origin of granite, with which so many ore-deposits are connected. All we are considering at the moment is the association of ore-deposition with the formation of igneous rocks at different geological epochs, which is far too common and widespread a phenomenon to be of other than genetic significance.

Some of our primary ores are in close and apparently genetic relation to volcanic lavas. For instance, masses of native copper were found in andesite of Devonian age in the Keelbottom River (Queensland), and there is reason to suppose that ore-mineral and host-rock are related. The small deposits of native copper in amygdales in the Permian trachybasalts on the South Coast of New South Wales are clearly comagmatic with the lavas, though doubtless the result of decomposition of cupriferous ferromagnesian minerals by deuteric solutions and subsequent deposition. It has been suggested that the silver-lead ores of Narlarla in West Kimberley (W.A.) are related to neighbouring volcanic plugs of Tertiary leucitic rock, and the quartz-veins containing gold, silver-lead and copper among the Upper pre-Cambrian Nullagine beds in the Pilbara district of Western Australia are considered to be comagmatic with the contemporaneous acid and basic lavas, while the gold of Cracow (Queensland) is thought by Denmead to have been introduced by andesitic magma in Mesozoic time.

The presence of ore-deposits in lavas may, however, be purely fortuitous, and it is probably so where gold is found in the Cambrian lavas or " diabases " of Heathcote (Victoria) and in the sheared Silurian andesites of Forbes, Blayney and Lucknow (N.S.W.).

Association of ores with hypabyssal intrusions, though far from common, is not unknown. In Western Australia there are many deposits of copper, lead, zinc and silver connected with basic dykes which have been variously assigned a late pre-Cambrian and a Palæozoic age but which may in fact belong to a number of different epochs. The copper of Blinman in the Flinders Ranges and other places in South Australia may have been introduced with certain basic dykes and other minor intrusions of Cambrian age. At Walhalla in central-eastern Victoria gold is closely associated with a swarm of dykes whose compositions range from intermediate to ultrabasic. On a much smaller and purely uneconomic scale are the auriferous pyrites of Mesozoic (?) quartz-dolerites and the gold associated with Tertiary (?) syenite-porphyries in Tasmania. The copper and gold deposits of Cobar (N.S.W.) seem to be proximately related to intrusions of quartz-porphyry, but these are in their turn probably co-magmatic with the granites cropping out at a distance of about 25 miles from the town.

It is clear that as with the volcanic rocks it may be hard to establish the existence of a genetic relation between ores and hypabyssal intrusions, since the jointing, cracking and shearing or faulting to which such rocks are liable may provide channels for ore-solutions not directly or at all connected with them.

By far the largest proportion of ore-deposits in the Commonwealth appear to be related to plutonic intrusions. They may be direct crystallizations or segregations of early-formed minerals, such as the chromite, platinum and osmiridium of the ultrabasic rocks, but for the most part they are of late deposition, crystallized in late differentiates or from late-magmatic or post-magmatic solutions, and chiefly in association with acid and intermediate rock-types. It is difficult to relate specific ore-minerals to specific rocks, but there is some evidence in the Commonwealth suggesting that gold accompanies granodiorite and copper and iron quartz-monzonite, while tin, tungsten, molybdenum, bismuth and antimony ores are of course found in general with the most acid types of granite. On the other hand examples have been reported of a zonal arrangement of ores around the margin of a bathylith according to the temperatures of formation, as at Heemskirk and other places in Tasmania and at Wolfram Hill in North Australia. In such circumstances the dominance of a particular metal in the ore-deposit is largely a function of the depth of erosion of the *terrain* or the distance from the edge of the intrusion.

The contention has been put forward that it is not necessarily correct to assume that a given primary ore-deposit is related to a neighbouring plutonic intrusion where the two are not in visible connexion. But around many bathyliths the normal contact-areole may have a surface-width of as much as a mile or more, and the deposition of relatively low-temperature ore-minerals from mobile magmatic solutions under pressure could surely have extended far beyond this limit. In any case the visible boundaries of its outcrop are not necessarily indicative of the underground extension of a bathylith, and the occasional presence of felspar and tourmaline in ore-bearing quartz-veins sufficiently attests their magmatic origin even when they cannot be traced into pegmatites.

Ores are seldom monometallic, and complex types are known in which quite a number of metals are of approximately equal importance, but it is probably true that in the majority of instances one or a few metals are dominant or predominant.

Epochs of Igneous Activity and Metallogenesis.

From the close connexion between ore-deposition and plutonic invasion it naturally follows that the great epochs of folding and plutonic invasion were also metallogenetic epochs. The bathyliths belong, broadly speaking, to two types, the synchronous or syntectonic and the subsequent or epitectonic. Opinions are divided as to the mode of emplacement of these, but the view is widely held that the first were formed largely through a process of transformation *in situ* of original sedimentary rocks by granitizing fluids, and that those of the second type represent the consolidation of bodies of liquid magma. However that may be, in the Commonwealth the synchronous type of bathylith was characteristic of the earliest known pre-Cambrian diastrophism, and of the late Ordovician and late Silurian orogenic epochs in eastern Australia. In general the other bathyliths are of subsequent type, though it would appear that some of those of late Middle pre-Cambrian age are synchronous. With both types ore-deposits are found to be associated.

Other possible metallogenetic epochs coincide with the times of injection of minor intrusions or with episodes of vulcanism, but, as already pointed out, these were not very important in Australia, and it can be said that with the vast majority of lava-flows and minor intrusions there have been found no signs of ore-deposits whatever. On the other hand the ores whose connexion with plutonic intrusions—bathyliths or stocks—is reasonably certain are legion.

All the forms of igneous activity referred to are related to geosynclinal deposition and deformation, but the volcanic and the hypabyssal may also be quite independent of it and be purely terrestrial in character.

In the geological record of the Commonwealth it is possible to discern nine epochs of folding and bathylithic formation accompanied by ore-deposition (see Table), and in addition a few epochs of hypabyssal intrusion and volcanic activity to which some ore-formation may be attributed.

Pre-Cambrian.

Probably for the world as a whole, as for Australia, the pre-Cambrian ores loom much larger than the sum total of all those of subsequent geological time. This may indicate, of course, that the pre-Cambrian was specially characterized by the introduction of ore-minerals, but it must be remembered that it embraced more than two-thirds of known geological time, and that it may have comprised several periods of deposition followed by epochs of folding and bathylithic injection, and punctuated by intervals of erosion sufficiently long to permit the complete elimination of all traces of the sediments. Professor Arthur Holmes has demonstrated by Pb/U determinations that at least seven distinct epochs of bathylithic injection and (presumably) orogenesis may be recognised for the pre-Cambrian. At present in the Commonwealth we have evidence of only three main periods of deposition and two main epochs of diastrophism and injection. The first or Pilbaran diastrophic epoch closed what we may call the Lower and the second or Houghtonian the Middle pre-Cambrian sedimentation. Probably the earliest metallogenetic epoch of which we have knowledge is that to which the gold ores of Kalgoorlie (W.A.) belong. There has been much controversy about the circumstances in which these ores were introduced, some workers relating them to the intrusions of the Younger Greenstones (dolerites) through their acid differentiates, a series of sodic porphyries and porphyrites, others preferring to connect them with hidden intrusions of granite similar to those occurring, with an accompaniment of auriferous quartz-veins, a few miles away. If the first view is correct, and it seems to have a good deal of justification, the epoch of metallization is probably Pilbaran, for the injection of the greenstones as sill-like masses seems to have heralded the Pilbaran folding, and indeed the rocks of the Younger Greenstone suite may be comagmatic with the granite-gneisses that were formed during the Pilbaran epoch. If on the other hand the gold is related to a granite, then its introduction most probably belongs to the Houghtonian epoch.

So far as we know, comparatively few ore-deposits are related to the Pilbaran intrusions. Apart from Kalgoorlie and a few other fields, such as Meekatharra and Wiluna, in which the gold ores are in greenstones and similar to those of Kalgoorlie, the only other known deposits which we can well assign to the Pilbaran epoch are the chromite contained in ultrabasic greenstones at Coobina in the north-west of Western Australia and the platinum which is present in rather insignificant amounts in certain altered basic or ultrabasic intrusions belonging to the Older Series in the Barrier Ranges near Broken Hill, New South Wales.

For Western Australia the Pilbaran and the Houghtonian were by far the most important epochs of ore-formation. During the second a great series of granitic bathyliths and stock-like masses were injected, with potassic and sodic pegmatites, and to them are related most of the gold occurrences of the State, together with a number of other ores, chiefly those of tin, iron, tungsten, molybdenum, tantalum and niobium, and minerals containing uranium, beryllium, lithium and the rare earths.

To the Houghtonian epoch also are assignable many ore-deposits outside Western Australia. In North Australia the gold of Buldiva, Pine Creek and a

number of other fields, the tin of Maranboy, the tantalum of Rum Jungle and the copper of Yeuralba all appear to be related to Houghtonian granites. Coming farther south we note that the gold of Tanami and The Granites and the auriferous hæmatite lenses of Tennant Creek are of the same age. At Hatches Creek are tungsten deposits, and in the Macdonnell Ranges the Oolgarna granites brought in the gold of the Winnecke, Arltunga and other fields, while the associated pegmatites have yielded beryl. Recently uranium has been reported from Hart's Range in the Eastern Macdonnells.

The chief primary ores of pre-Cambrian age in South Australia are the copper deposits of Wallaroo and Moonta, whose parent magma appears to have been that which produced the Houghtonian granites and pegmatites with which they are associated. A little uranium is associated with the copper ores. The uranium ores of Mt. Painter, in the extreme north of the Flinders Ranges, are in granitic igneous intrusions, but whether these are of Houghtonian age or later is still in dispute, as is likewise the age of the granites in the east of the State with which the radio-active ilmenite of Olary is associated. Traces of uranium minerals have also been noted in Houghtonian (?) pegmatites in Eyre Peninsula. Apart from rutile and monazite which are found in titaniferous pegmatites in a few places, there do not appear to be any further pre-Cambrian ores of note in South Australia.

Across the border the great silver-lead-zinc deposit of Broken Hill, with copper, gold, cadmium and other minor constituents, is most reasonably regarded as comagmatic with Houghtonian granites like those of Mundi Mundi, and farther to the north in the Barrier Ranges are pegmatites with tinstone, wolfram and amblygonite. The other easterly projection of the Great Western Plateau contains the copper and iron deposits of the Cloncurry region including those of the Cloncurry district, Mt. Philp, Mt. Oxide and a number of other outlying fields, together with the silver-lead and copper lodes of Mt. Isa. All these appear to be related to the Cloncurry and Templeton River granites. Much farther north the silver-lead of Lawn Hill is probably in part of the same age but perhaps partly younger. Rutile, beryl, monazite and other rare minerals occur in pegmatites west of Mt. Isa, related to the Templeton River granite. East of Cloncurry the pre-Cambrian disappear under Mesozoic beds, to emerge in the Etheridge and other goldfields, where some of the gold at all events seems to be pre-Cambrian and probably Houghtonian.

The possibility that some of the gold, silver-lead and copper of Western Australia, and particularly of the Pilbara area, is related to contemporaneous lavas of Nullagine (Upper pre-Cambrian) age and basic dykes of latest pre-Cambrian has already been referred to. The presence of these ores may be regarded as marking a minor pre-Cambrian metallogenetic epoch in Western Australia.

Cambrian.

Upper pre-Cambrian seems to have passed into Palæozoic time without any orogenic break, and sedimentation continued till the end of the Middle Cambrian epoch. Most of it occurred in the great Central Basin, which included the sites of the Mt. Lofty and Flinders Ranges in South Australia and extended east into New South Wales and Queensland, and south and south-east to Victoria and Tasmania. In the north it embraced much of Northern Territory (including the Macdonnell Ranges) and spread into East Kimberley. At this time also the Tasman geosyncline was probably initiated in eastern Australia. During the Tyennan epoch, shortly after the close of the Middle Cambrian, Upper pre-Cambrian and Cambrian rocks were folded together, and there was injection of granites, pegmatites and quartz-veins along the southern and eastern Mt. Lofty Ranges and to the south-east into the far west of Victoria. The intrusions

seem to have extended north to the north-east of the Macdonnell Ranges, and granite was injected into the Upper pre-Cambrian rocks in the far north-west of New South Wales, in the Koonenberry, Wertago and Nuntherungie Ranges and at Tibooburra. At the same time granites, granite-porphyries and syenites invaded the Lower and Middle Cambrian and Upper pre-Cambrian rocks of northern and western Tasmania at Middlesex Plains, Mt. Darwin and elsewhere.

These irruptions of magma were responsible for a limited amount of ore-deposition. They probably brought in the copper of the Mt. Lofty and Flinders Ranges fields, as at Burra, Kapunda, Balhannah, Callington, Blinman and Yudnamutana, and the gold of Mt. Grainger and other goldfields. The copper, however, may in part have come in with minor basic intrusions that intersect the Cambrian and Upper pre-Cambrian rocks. It has been argued that the magmas responsible for the radio-active ores of Mt. Painter and Olary invaded Upper pre-Cambrian rocks, and if so they are probably Tyennan. Some beryl-bearing pegmatites in the eastern Mt. Lofty Ranges may be of the same age, and so may the tungsten of Wauchope Creek in Central Australia.

In the far north-west of New South Wales the granites introduced copper and gold, and it may be that some of the Lawn Hill silver-lead ores of North Queensland, which are in gently folded Cambrian rocks, were emplaced during the same epoch.

Mineralization related to the Tyennan granites of Tasmania was not important or extensive; in fact only some copper and the iron-ores of the Jukes-Darwin field have been referred, and with some doubt, to their entry. If, however, as has been suggested, the ultrabasic intrusions of western Tasmania are Cambrian, then chromium, nickel and osmiridium minerals are to be added to the Tyennan ores.

On the whole this metallogenetic epoch was far from spectacular, except in South Australia, where more copper has been mined than in any other State.

Ordovician.

After the Cambrian period by far the most important metallogenetic events in the geological history of the Commonwealth occurred in eastern Australia, which was the site of the Tasman geosyncline. At the close of the Ordovician sedimentation came the Benambran epoch of folding and formation of synchronous batholiths of somewhat acid granites with pegmatites. Diastrophism affected a broad median zone running through eastern Victoria and the highlands and Western Slopes of New South Wales, which must have been prolonged into Queensland. Two chief belts of granitic batholiths are known, the more westerly of which, about 100 miles wide, starts in the highlands of eastern Victoria, passes through Albury and the Upper Murray country, to the east of Wagga, and north through Junee as far at least as a point 20 miles west of Condobolin. Some gold and tin in Victoria and in south-eastern New South Wales seems to have been introduced with the granite and pegmatites, and gold further north at Junee Reefs and Sebastopol, but this region was subjected to at least three subsequent epochs of folding and plutonic invasion, and it is by no means easy to determine beyond doubt the respective ages of all the ore-deposits. It is possible that some of the tin-ores of the Western Slopes, as at Mt. Tallebung, Buddigower and elsewhere, are Ordovician, but information on the point is lacking.

Silurian.

At the end of the Silurian Period during the Bowning epoch the geosyncline suffered further diastrophism except for a narrow zone in the extreme west. Synchronous batholiths and porphyry lenses associated with the folding are widespread in the Eastern Highlands and Western Slopes of New South Wales

and extend into eastern Victoria. We find them in New England east of Armidale and south as far as Walcha, in the Central Highlands at Cow Flat and elsewhere south of Bathurst, at Crookwell and Wheeo north of Goulburn and probably also as far west as Nymagee. They are also seen at Breadalbane and Gunning, east and west of Lake George, about Adelong and Batlow, near Grenfell, in the Australian Capital Territory and south to Cooma, on the Kosciusko plateau, near Delegate, north of Albury and across the border into Victoria to the Omeo district. Many of the rocks are hybridized and of the composition of quartz-diorites. Gold seems to be genetically related to many of the gneissic granites and porphyries in Victoria and in New South Wales, as at Adelong, Cooma, Michelago, Tuena, Wyalong and perhaps too at Hillgrove (New England). Copper is known from Cow Flat, iron ore occurs at Breadalbane west of Goulburn, and a series of small deposits of iron and copper ores borders the Murrumbidgee bathylith on its eastern side from the Cotter junction south to Cooma.

To the Bowning epoch are usually assigned the sheets of ultrabasic intrusives and serpentinized peridotites, pyroxenites, etc., which form two long sub-meridional belts on the South-Western Slopes, one running through Gundagai and the other to the east of it. A certain amount of gold has been yielded by these intrusions, but it is very doubtful if they are more than host-rocks, though they may have been comagmatic with granites and porphyries which were the probable ore-carriers. Chromite has been got from the ultrabasic rocks at several places. The platiniferous serpentine of Fifield is also possibly late Silurian.

No ore-deposits of late Silurian age have been definitely recognised in Queensland, though it is by no means unlikely that such exist. They may, of course, be largely hidden beneath the sediments of the Great Australian Artesian Basin.

Middle Devonian.

Tasmania and central Victoria escaped the Bowning orogeny, and Silurian and Devonian rocks there were deformed together during the Tabberabberan orogeny that brought the Middle Devonian epoch to an end. The belt of folding must have continued north into New South Wales, where we find a number of plutonic masses intrusive into Silurian and overlain by Upper Devonian rocks, which seem to belong to this epoch. They are of granite and/or granodiorite, and of subsequent type, and apart from field-relations there is no certain way of distinguishing between them and the Carboniferous intrusions, which resemble them petrologically and whose region of intrusion overlapped theirs.

No intrusions of this age are certainly known in Queensland, though the belt of folding must have extended into that State. The gold-bearing granites of Charters Towers were thought by Jack to be overlain farther north by Upper Devonian beds, and if so the gold of this field and of Ravenswood and other adjoining fields may be Middle Devonian. In New South Wales Andrews recorded from east of Parkes a granite which must be Tabberabberan, and not improbably it or an allied intrusion was responsible for the mineralization of the Forbes-Parkes area, in which the auriferous solutions took advantage of shear-zones in the Silurian sediments and contemporaneous andesitic flows. It may be with a granite of the same age that the wolfram of Yeoval is connected. In the Cobar-Nymagee-Mt. Hope area there are massive granites and porphyries locally crushed, which are probably comagmatic, intrusive into Silurian and overlain by Upper Devonian beds and therefore Tabberabberan. Their magma is most likely to have been the vehicle for the gold, copper and other ores of the region.

A composite bathylith of granite and granodiorite with marginal quartz-porphyries and quartz-porphyrites stretches north for some 50 miles from Bungonia near Goulburn to Wombeyan and beyond. There is but little mineralization known to be connected with it, but the silver-lead ores of the old Carrington mine near Marulan may be related to it, and so may the complex ores of the Tolwong mine on the Shoalhaven River.

In the Yass-Burrinjuck area are granites and porphyrites intrusive into Silurian and Middle Devonian rocks, and they are perhaps to be regarded as Tabberabberan and are probably responsible for the small silver-lead and copper deposits of the area. The intrusions seem to be continued south to the Tumut River, Yarrangobilly, Lobb's Hole and the country at the head of the Goodradigbee River, where small deposits of copper and silver-lead are associated with them. Farther north the wolfram of Frogmore is in granite of possibly the same age. The great bathylith running from Kiandra past Adaminaby and through Berridale, the Kosciusko plateau and Dalgety into Victoria is most likely Tabberabberan though perhaps younger. Gold, copper and a little wolfram are found with it.

In eastern and central-eastern Victoria many of the big intrusions may be Tabberabberan, but they are not easily separable from those of Carboniferous age. The diorites, intrusive into Lower Devonian beds, which brought in the gold of the Diamond Creek, Queenstown and Warrandyte fields, north-east of Melbourne, are probably of this age, and so is the remarkable swarm of dykes of intermediate to basic composition which follows the strike of the Silurian and Lower Devonian (?) beds of the Walhalla synclinorium in eastern Victoria ; these are clearly related to the folding of the beds, which is Tabberabberan. The auriferous quartz-veins so abundant both in the dykes and in the folded sediments are comagmatic with the dyke-rocks. The gold-bearing granodiorites and porphyrites of the Strathbogie Ranges also seem to be Middle Devonian. As for the massive granites and associated gold deposits among the Ordovician schists of the north-east, it is very hard to tell their age ; some of them are possibly Tabberabberan, and the same may be said for the copper and silver-lead at Buchan and Mt. Deddick.

In western Tasmania a series of granodiorites, porphyries and porphyrites, massive but passing into schistose phases, invades strata as high as Silurian and Lower Devonian, and may provisionally be regarded as Middle Devonian. With them came the deposits of copper, zinc, lead, silver and antimony in the Mt. Lyell, Zeehan, Rosebery and other fields.

Lower Carboniferous.

The Devonian passed into the Carboniferous Period with no orogenic interruption, but during and at the end of the Lower Carboniferous came the important Kanimblan epoch of folding, intrusion and metallogenesis. The whole of the Tasman geosyncline was affected save for a belt on the east coast of Queensland and New South Wales, and Kanimblan intrusions appear at intervals from the tip of Cape York Peninsula to the most southerly point of Tasmania. They show much magmatic differentiation and include very acid granitic types. With them are associated the gold deposits of Cape York Peninsula, and possibly those in the Hodgkinson and Herberton fields, at Croydon and Mt. Emu, and some of those of the Etheridge field. The extensive massive granites of the Charters Towers, Ravenswood and other neighbouring goldfields may belong to this epoch, though, as suggested above, they may be older. With the acid granites are associated the tin, wolfram and molybdenum ores of the Herberton region, and in the Herberton and Chillagoe fields there are silver-lead and copper. The Clermont and Mt. Wyatt goldfields may also be Kanimblan. There is some regional overlap between the Kanimblan and late

ORE REGIONS, PROVINCES AND DISTRICTS.

During any given metallogenetic epoch there was in general a variety of ores introduced. These, however acquired, may be looked upon as an integral part of the magma, intrusive or extrusive, with which they are associated. For the igneous rocks petrological kindreds and petrographical provinces have been determined by the prominence of certain elements or certain minerals of a common age in the component rocks, and in a similar way it may be found possible to distinguish ore provinces and ore regions. As it appears to be understood in this country, the term " ore province " has a purely geographical connotation, the question of age being ignored, perhaps because of a tacit assumption that the same magma with the same ore-constituents persisted under a given region throughout long intervals of geological time. But for the igneous rocks it has been shown that the petrological character of extrusions and intrusions has changed from time to time, and it does seem possible that a similar state of affairs may obtain for ore-deposits. Combining the considerations of space and time we may define an ore region as a major area within which

Fig. 2.—Pre-Cambrian ore regions and provinces.

ore-deposition occurred during a particular metallogenetic epoch. In general there will be a big variety of ores in such a region, but these are often segregated, and it may be possible to recognize smaller areas, either parts of an ore region or independent entities, characterized by dominance or predominance of ores of one or more elements ; these we may call ore provinces, and even smaller and more specialized areas may be recognizable which may constitute ore districts. Since ore-deposition may have recurred several times in any given area, there may be overlapping of ore regions, provinces or districts of different geological epochs, and only a very intensive field-study will serve to differentiate them.

In Western Australia it is hardly possible to separate the pre-Cambrian ore regions of Pilbaran and Houghtonian age, but in the second of these epochs a large part of the State helped to constitute a very large ore region characterized by a general dominance of gold, with copper and iron almost as widely though by no means so abundantly distributed (Fig. 2). Simpson showed that in a coastal belt about 250 miles wide from West Kimberley to Norseman and Esperance there is a province abounding in lithium, beryllium, lanthanum,

cerium, tantalum and tungsten minerals. Some of these characterize separate ore districts; for instance tin and tantalum are associated in the south at Greenbushes, in the centre at Poona and Coodardy, and in the north at Moolyella, Wodgina and elsewhere in the Pilbara goldfield.

The pre-Cambrian ore-regions extend into North Australia, where gold and tin-tantalum provinces can be recognized, and the gold distribution extends far south into Central Australia.

In South Australia and western New South Wales there are provinces rich respectively in titanium and silver-lead and zinc, and the Moonta-Wallaroo area is a copper province. The Cloncurry ore-province of western Queensland is essentially a copper one with local concentrations of silver-lead and iron.

The Tyennan intrusions of Upper Cambrian time established an important copper province in the Mt. Lofty and Flinders Ranges, with gold and subsidiary ores of bismuth, molybdenum and uranium, which are in part restricted to separate districts. A copper-gold province was also constituted in the far
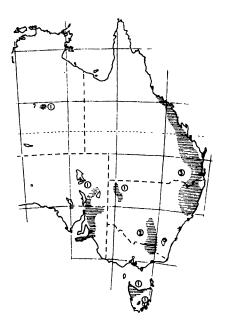
Fig. 3.—Upper Cambrian (1), Late
Ordovician (2), and Late Permian
(3) ore regions.

Fig. 4.—Late Silurian (1)
and Late Cretaceous (2)
ore regions.

north-west of New South Wales, and if the ultrabasic intrusions in the western half of Tasmania are of the same age, then this area also formed an Upper Cambrian ore-province with chromium, nickel and osmiridium (Fig. 3 (1)).

A late Ordovician (Benambran) gold-tin province seems to have been established in north-eastern Victoria and the adjoining parts of New South Wales, and may have extended in a north-north-westerly direction along the Western Slopes towards Condobolin (Fig. 3 (2)). The same general region may also have been a gold province in the late Silurian, and there were gold provinces and districts in the Central and Southern Highlands and on their western slopes as at Tuena, Adelong and Wyalong, also perhaps in New England. A long, narrow, iron-gold-copper province bordered the Murrumbidgee bathylith on the east and a linear province was constituted by the chromite and nickel of Gundagai, Berthong, Wallendbeen and other centres (Fig. 4 (1)).

To the Tabberabberan ore region of New South Wales and Victoria belong the gold-copper deposits of the Cobar-Nymagee-Mt. Hope and the Forbes-Parkes provinces and the gold province of central-eastern Victoria from Queenstown and Warrandyte to Walhalla and Wood's Point. There was possibly a contemporary gold-copper province in western Tasmania and a gold province about Charters Towers (Queensland) (Fig. 5).

During the Kanimblan epoch eastern Australia contained a number of ore regions wherein several ore provinces and districts co-existed (Fig. 6). In the North Queensland region, for instance, which is broadly characterized by gold, there is the important Herberton-Chillagoe province with tin, silver-lead, copper, molybdenum and tungsten. To the same epoch may belong the Charters Towers (gold) and Clermont (copper-gold) provinces. The tin deposits of the country west of Cooktown mark a separate ore district. A linear iron province stretches along the coast between Mackay and the latitude of Maryborough.

Fig. 5.—Late Middle Devonian
ore regions and provinces.
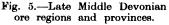
Fig. 6.—Ore regions of late
Lower Carboniferous time.

The southern region contains copper and gold widely distributed in the Central and Southern Highlands and Western Slopes of New South Wales, and a tin province in which the Ardlethan deposits are prominent. Small gold districts are seen at Yalwal and Moruya, and the Bega bathylith with its continuation into Victoria is marked by gold in the north and by molybdenum and bismuth farther south. The Victorian part of this region is essentially a great gold province in the western and central-eastern parts, with a few local concentrations of other metals, as of antimony at Heathcote and tin in the south-east.

At this time, too, an ore-province was formed in the northern half of Tasmania, wherein tinstone is the dominant economic mineral, with silver-lead, tungsten, bismuth and gold forming concentrations in various districts. This province is linked to Victoria through the King Island scheelite and the tin of Wilson's Promontory and, if the ultrabasic intrusions are Carboniferous and not Cambrian, by the osmiridium occurring at Waratah Bay.

TENTATIVE CORRELATIONS OF OROGENIC, INTRUSIVE AND METALLOGENETIC EPOCHS IN THE COMMONWEALTH OF AUSTRALIA.

EPOCH.	WESTERN AUSTRALIA.	NORTHERN TERRITORY.	SOUTH AUSTRALIA.	TASMANIA.	VICTORIA.	NEW SOUTH WALES.	QUEENSLAND.
Lower Pre-Cambrian (Pilbaran).	? Au of Kalgoorlie, Wiluna, etc. ? Cr of Coolbna in Ophthalmia Ra.	—	—	—	—	Pt. in Barrier Ra.	—
Late Middle Pre-Cambrian (Houghtonian).	An associated with granite and quartz in most goldfields. Cu, Ag-Pb and Fe, Sn and Ta with Be at Greenbushes, Moolyella, Wodgina, etc. Rare earths and U in pegmatites.	Au, Cu, Ag-Pb, etc., of Pine Ck. and Daly R. districts, Yeeramba, Tanami, The Granites, Tennant Ck. and Arltunga and Winnecke fields. Sn at Maranboy, Bulliva, Yeuralba, etc., and with Ta at Hynes Harb., Rum Jungle and Finniss R. W., etc., at Pine Ck. and Hatches Ck. Be and U of Macdonnell Ras.	Cu, Au etc. of Wallaroo and Moonta, Thecoola, Eyre Pen., Olary, etc. Tl, Be and Th in pegmatide at Normanville, Strathalbyn, etc. ? Some Au of Mt. Lofty Ras. U of Olary.	—	—	Ag-Pb, Zn and Cu of Broken Hill, Silverton, Thackaringa, Yanco Glen, etc. Sn, W and Li of Euriowie, Kantappa, etc.	Cu, Au, Ag-Pb, Zn and Fe, etc, of Cloncurry region, as at Cloncurry, Mt. Isa, Mt. Philip and Mt. Oxide. Au and Cu of Gilbert, Wodgar and Einasleigh fields. (?) Fe of Chaudie R. Ti, Ta and Be of Mica Ck. near Mt. Isa.
Upper Cambrian (Tyennan).	(?) Cu in valley of Ashburton R. ? Ag-Pb of Brueside in Pilbara goldfield.	Cu of Wollogorang-Redbank field. ? W of Wauchope Ck.	Cu, Au and Bi at Burra, Callington, Kapunda, Mt. Grainger, Blinman, Yudnamutana and elsewhere in Mt. Lofty and Flinders Ras. Ag-Pb of Glen Osmond, Callington, Strathalbyn, Kangaroo I., etc. ? U of Mt. Painter.	? Cu of Heazlewood and Fe of Jukes-Darwin field. ? Cr, Ni and Os associated with serpentine at Adamsfield and in the west and north-west (may be Kanimblan).	? On at Waratah Bay.	Cu and Au at Wertago, Koonenberry, Mt. Browne, Tiboobura, etc.	? Some Ag-Pb and Zn at Lawn Hill.
Late Ordovician (Benambran).	—	—	—	—	? Sn at Eskdale, Tallandoon and Mt. Wahra in the north-east, and ? Au at Bethanga, etc.	Au at Sebastopol and Junee Reefs. ? Sn at Holbrook, Batidale and Jingellic and perhaps at Mt. Tallebung, etc.	—
Late Silurian (Bowning).	—	—	—	—	? Au in north-east at Granya.	An at Adelong, Gundagai, Wyalong and at Trunkey, Tuena, Burraga and Hockley. Cu at Cow Flat. Au, Cu and Fe along east of Murrumbidgee bathylith. Cr of Coolac, Gundagai, Berthong, etc. Pt. at Fifield.	—
Middle Devonian (Tabberabberan).	—	—	—	(?) Cu, Au, etc., at Mt. Lyell, Jukes-Darwin, etc., on West Coast.	Au at Queenstown, Diamond Ck. and Warrandyte, N.E. of Melbourne. Au and Cu of Walhalla-Wood's Point belt. ? Cu and Ag-Pb of Mt. Deddick and Buchan. ? Sn of Cudgewa in N.E.	Cu and Au in Cobar-Canbelego, Mt. Hope, Nymagee, Tottenham and Condobolin areas. Au at Forbes and Parkes. Cu and Ag-Pb in Yass-Burrowa district. ? Au at Kiandra, Tumbarumba, Gundagai and Young. ? W at Yeoval, Frogmore and Derribid. Ag, Cu and Sn of Marulan and Tolwong.	? Au of Charters Towers, Cape R. and Ravenswood (may be Kanimblan).
Late Lower Carboniferous (Kanimblan).	—	—	—	Ag-Pb, Zn, Cu, Sn, W, Sb, Bi and Au of Zeehan, Renal-Rosebery, Mt. Farrell, Dundas, Moina, Middlesex, Waratah and Stony Ck. and of the north-east. Fe of Blythe R. W of King I.	Au of Stawell and of the fields of the central-west, e.g. Bendigo, Ballarat, Daylesford, etc., also of Costerfield (with Sb). Some Sn in the N.E. and at Wilson's Promontory. W at Maryville and Warburton and Mo at Yea, Maldon, Mt. William, etc.	Au, Ag-Pb, Fe, etc., of Hill End, Orange, Bathurst, Blayney, Lyndhurst and Wellington districts. Mo of Yetholme. Ag of Yerranderie. Au, Cu and Zn of Captain's Flat. Bi, Au and Mo of the Bega bathylith. Yalwal, Monya, Araluen and Braidwood. ? Sn of Buddigower, Kikoira, Ardlethan and Pulletop.	Au of Chatdie R. and other fields in C. York Pen. and of Palmer R. and Mt. Wyatt. Sn, Ag-Pb, Cu, W, Mo, Bi, etc., of Chillagoe and Herberton districts, Star R., Cooktown, Silver Valley, Einasleigh, Cardross, etc. Au and Cu of Clermont. Au, Cu and Ag-Pb of Kilkivan. Au, W and Mo of Hodgkinson Field. Fe of Chillagoe and in Rockhampton-Gladstone belt.
Late Permian (Hunter-Bowen).	—	—		—	—	Au, Cu, Sn, Mo, W, As, Sb, etc., of New England and the North Coast, as at Drake, Kingsgate, Inverell, Hillgrove, Emmaville, Deepwater, Coramba, Valla, Cr, etc., of Great Serpentine Belt, New England and Port Macquarie.	Au and Cu of Mt. Morgan, Mt. Chalmers, Mt. Perry, Mt. Flora, Cania, Cawrai, the Normanby, Eungella, Calliope, Gympie and other fields. Sn, W and Mo of Stanthorpe. Au and Ag-Pb of Kingsgate. Ag of Silver Spur. ? Au of Cracow in part. Au, Fe and Bi of Biggenden. Cr, Ni and Co in serpentine at Pine Mt. and Killkivan and in Rockhampton district.
Late Cretaceous (Maryborough).	—	—	—	—	—	—	Au at North Arm, Marodian and Yorkeys, Au and Ag-Pb at Montdale. Au and Ag at Mt. Biggenden. ? Some Au, Cu, Sn, W and Mo of Kenagara. Sn at Cracow. Cu and Pb in Maryborough area.

resources of ores were dwindling, and stressed the need for an intensive search for new deposits.   If a detailed study could be made of the extent and boundaries of the known ore regions, provinces and districts, and of the nature of their contained ores, with due regard to the epochs as well as the places of ore-intro-duction, much time and energy might be saved by directing the search to the most favourable places.   Such a study would be no doubt lengthy and laborious, but at all events the policy would be systematic and scientific, and I venture to suggest that in the long run it would be justified by results.

REFERENCES.

Andrews, E. C., 1923. Geographical Distribution of Ore Deposits in Australia. *Econ. Geol.*, 18, 1.

Ball, L. C., 1923. Ore Provinces in Queensland. *Proc. Pacific Sci. Cong. (Aust.)*, 1, 790.

Edwards, A. B., 1943. Copper Deposits of Australia. *Proc. Aust. Inst. Min. Met.*, 130, 105.

Hills, E. S., 1947. The Metalliferous Geochemical Zones of Australia. *Econ. Geol.*, 42, 478.

Jones, O. A., 1947. Ore Genesis of Queensland. *Proc. roy. Soc. Q'ld.*, 59, 2.

Prider, R. T., 1945. Igneous Activity and Ore-Formation in Western Australia. *J. roy. Soc. W. Aust.*, 31, 43.

Simpson, E. S., 1939. Mineral Provinces and Metallogenetic Epochs in Western Australia. *J. roy. Soc. W. Aust.*, 25, 207.

STILLWELL, F. L., 1923. Correlation of Ore Deposits in Australia. *Proc. Pacif. Sci. Cong. (Aust.)*, 1, 796.

Waterhouse, L. L., 1923. Ore Provinces in New South Wales. *Proc. Pacif. Sci. Cong. (Aust.)*, 1, 787.

NITROGEN IN OIL SHALE AND SHALE OIL

XI. Nitriles in Cracked Shale Gasoline.

By Geo. E. Mapstone, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

In an unsuccessful attempt to detect thiazoles in the tar bases isolated from cracked shale gasoline by reductive cleavage with sodium and alcohol, followed by the detection of a mercaptan (Morton, 1946), it was observed that an appreciable amount of ammonia was liberated. Since this ammonia was free from both primary and secondary amines, it was possible that it had been derived from the hydrolysis of some constituent of the bases rather than by the reduction. Nitriles are present to a small extent in crude shale oil (Mapstone, 1949), and it would also be possible that small amounts may be formed during the thermal cracking of the crude oil for the production of the gasoline (Mapstone, 1948). Traces of hydrogen cyanide have been found in the cracked shale gasoline (Mapstone, 1946) and it may be considered as the simplest nitrile—formonitrile. The work described here was therefore carried out to determine, if possible the, amount of nitriles present in the bases.

DETERMINATION OF AMMONIA FROM THE HYDROLYSIS.

Barta and Marschek's observation that pyridine and its homologues could be separated from ammonia by distillation from a citrate buffer at pH 3·0 (Barta and Marschek, 1937, 1938) was used as a basis for the determination of the amount of ammonia liberated during the hydrolysis. Two hundred millilitres of redistilled tar bases isolated from the acid sludge from the treatment of the gasoline (Mapstone, 1947) were hydrolysed by 50 ml. of 10% sodium hydroxide solution in a distillation flask fitted with a reflux condenser and inclined so that no condensate could collect in the side arm. Since ammonia has a much lower boiling point than the tar bases, it could be distilled off continuously as formed. However, with the very small quantity of ammonia involved it was necessary to reduce to a minimum the amount of the pyridine homologues that distilled with the ammonia, as well as to provide a carrier to transfer the ammonia from the condenser to the absorption solution. This was achieved by periodically purging the contents of the condenser into 100 ml. of sodium phosphate-citric acid buffer of pH 3·0 (Hodgman, 1940) by passing a stream of ammonia-free air through the side arm of the flask. By reducing the heating rate so that the level of refluxing vapours was just above the side arm at the time of purging, the amount of pyridine homologues carried over with the ammonia was kept between 5% and 30% of the amount of ammonia evolved.

When the hydrolysis was considered to be complete after one to one and a half hours, 10% to 20% of the buffer solution were distilled into 100 ml. of 1% boric acid, and the pyridine homologues that had been absorbed along with the ammonia determined by titration of the distillate with 0·1 N acid. The ammonia was then determined by rendering the remainder of the buffer solution strongly alkaline with 40% sodium hydroxide solution and distilling into a fresh boric acid solution.

DETERMINATION OF ORGANIC ACIDS FROM THE HYDROLYSIS.

When cool, the dark brown layer of sodium hydroxide solution was separated from the tar bases, rendered strongly acidic with sulphuric acid, and distilled. The distillate was titrated with 0·1 N carbonate-free sodium hydroxide to a phenolphthalein end point for the determination of the organic acids. An appreciable amount of phenols was also present in the distillate.

The solutions containing the organic acids from all the analyses were bulked, acidified and distilled. The distillate was extracted with carbon tetrachloride to remove the phenols, neutralized with barium hydroxide, and evaporated to dryness. The dry barium salts were refluxed with ethyl alcohol and concentrated sulphuric acid ; the sweet odour of the ester thus formed confirmed that the acids were organic. Three of five opinions were definite that the ester smelt like pineapple (ethyl valerate), and would therefore suggest that there was some valeronitrile (b.p. 141° C.) present in the bases.

DISCUSSION OF RESULTS.

Two samples of the bases were examined : one which had been isolated about four years previously, and another which was freshly isolated for this work. In each case the analysis was carried out in duplicate. The agreement between the amounts of ammonia and organic acids obtained (Table 1) indicates that they were liberated in equivalent quantities during the hydrolysis, and that their precursors were most probably nitriles.

The small amount of nitriles thus found to be present in the tar bases is equivalent to approximately 0·05% by volume (calculated as valeronitrile). Since the bases are present to an extent of only 0·3% by volume in the cracked shale gasoline, the nitriles found are equivalent to approximately 1·5 p.p.m. in the gasoline. In connection with some other work, it was found that a single wash with 10% of concentrated sulphuric acid completely extracted 0·5% of benzyl cyanide from crude shale oil, so it is probable that the whole of the nitriles in the cracked shale gasoline were concentrated in the sludge from which they would be isolated along with the tar bases. The actual nitrile content of the untreated gasoline would no doubt be somewhat higher than the 1·5 p.p.m. found here as portion will probably have been hydrolysed by the caustic washes given the gasoline prior to acid treatment, and during the recovery of the bases from the acid sludge.

TABLE 1.

Hydrolysis of Bases.

(Results as milliequivalents per litre of bases.)

Bases.				Ammonia.	Organic Acids.
Old	..	..	..	6·0	7·1
Old	..	..	..	3·9	2·7
Old average	..	..	..	5·0	4·9
Fresh	..	..	..	5·1	7·9
Fresh	..	..	..	6·9	5·7
Fresh average		..	..	6·0	6·8

SUMMARY.

The amounts of ammonia and organic acids obtained by the hydrolysis of the tar bases isolated from the acid sludge from the treatment of the gasoline indicate the presence of about 1·5 p.p.m. of nitriles in the original gasoline.

REFERENCES.

Barta, L., and Marschek, Z., 1937. *Biochem. Z.*, **293**, 118-120.

———————————————— 1938. *Chem. Abs.*, **32**, 967.

Hodgman, C. D., 1940. " Handbook of Chemistry and Physics ", Chemical Rubber Publishing Co., Cleveland, Ohio, 24th Ed.

Mapstone, G. E., 1947. *Petroleum Refiner*, **26**, 574-576.

——————————— 1948. THIS JOURNAL, **82**, 91-95, 96-106.

Mapstone, G. E., and McLaren, C. B., 1946. *Petroleum Refiner*, **25**, 49-52.

——————————— THIS JOURNAL, **83**. See part I.

Morton, A. A., 1946. " The Chemistry of Heterocyclic Compounds ", McGraw Hill Book Co., New York, pp. 406-9.

THE CYCLIZATION OF ANILS OF β-KETO-ALDEHYDES.

By G. E. CALF
and E. RITCHIE, M.Sc.

It is well known that anils of β-diketones are readily cyclized by acidic reagents to 2 : 4-disubstituted quinolines (e.g. Combes, 1888 ; Roberts and Turner, 1927).   It would therefore be expected that anils of β-keto-aldehydes would form 4-substituted quinolines, but so far attempts to effect such cyclizations have been unsuccessful (Claisen and Fischer, 1888 ; Thielpape, 1922) or have given very low yields (Romet, 1935).   Borsche (1910) also failed to convert 1-(phenyliminomethyl)-*cyclo*hexan-2-one (I) to the tetrahydrophenanthridine (II) by heating it with concentrated sulphuric acid at 100°, obtaining only the *p*-sulphonic acid of I and a similar result was obtained from the *m*-hydroxy derivative of I.   However, since the successful cyclization of I would lead to an attractive phenanthridine synthesis, we have studied this reaction more fully.

I.   II.

Numerous experiments were carried out in which I was treated with sulphuric acid of various concentrations at temperatures between 0° and 100°, but in each case it was either recovered unchanged or was sulphonated, and similar results were obtained with the methyl- and methoxy-derivatives of I.   However, it was found that if these anils were refluxed with phosphorus oxychloride they were converted in 20–25% yield to bases which were identified as derivatives of 1 : 2 : 3 : 4-tetrahydroacridine (III).   The same substances were formed, but in somewhat lower yields, by heating the anils with phosphorus pentoxide at 250° for a short time.   The formation of these substances is best explained by the equations

III

which were originally suggested by Petrow (1942) to account for the formation of III when I was heated with aniline hydrochloride and zinc chloride in alcoholic solution.

The failure of anils of β-ketoaldehydes to cyclize normally has been explained by assuming that they exist in the *trans* configuration IV, which would be unfavourable to cyclization, rather than in the favourable *cis* configuration I. (Petrow, *loc. cit.* ; Thielepape, *loc. cit.*)

IV.   V.

However, no direct evidence for this assumption has been adduced and two strong objections may be made against it.   Firstly, every analogy suggests that the anils are hydrogen bonded resonance hybrids, one of the chief contributing structures of which is shown by V, and which does have a configuration favourable to cyclization.   Secondly, whatever the configuration of the anil itself may be, there is no reason to suppose that this configuration would be preserved in concentrated sulphuric acid (the usual cyclizing reagent).   It appears then that some other explanation for the failure of anils of β-ketoaldehydes to cyclize smoothly must be sought.

EXPERIMENTAL.

The anils used in the following experiments were prepared by condensing *formyl*-cyclohexanone with aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, *o*-anisidine and *p*-anisidine respectively, in alcoholic solution (Petrow, *loc. cit.*).

Cyclization by Phosphorus Oxychloride.

The anil (10 g.) was gently refluxed with phosphorus oxychloride (30 c.c.) with exclusion of moisture for one hour.   After cooling, the reaction mixture was poured into ice and water with vigorous stirring and when reaction ceased, filtered from resinous products.   The filtrate was basified, extracted with ether and the product eventually isolated by distillation under reduced pressure in 20–25% yield.   Final purification was effected by recrystallization from light petroleum.

Cyclization by Phosphorus Pentoxide.

An intimate mixture of the anil (10 g.) and phosphorus pentoxide (30 g.) was immersed in an oil bath maintained at 250° for fifteen minutes.   After cooling, the reaction mixture was worked up as above, giving the tetrahydroacridine in about 10% yield.

The following tetrahydro-acridines, which were identified by their melting points, analyses (not quoted) and the melting points and analyses of their picrates (not quoted) were prepared by both of these methods : tetrahydroacridine m.pt. 56° (55°–56°), picrate m.pt. 220° (222°) ; 9-methyltetrahydroacridine, m.pt. 77° (77°–78°), picrate m.pt. 215°–216° (215°–216°) ; 8-methyltetrahydroacridine, m.pt. 100° (100°–101°), picrate m.pt. 186° (189°–190°) ; 7-methyltetrahydroacridine, m.pt. 62° (61°–62°), picrate m.pt. 189° (189·5°–190·5°) ; 9-methoxytetrahydroacridine, m.pt. 122° (121·5°–122·5°), picrate m.pt. 204° (206·5°–207·5°), and 7-methoxytetrahydroacridine, m.pt. 90° (90°–91°), picrate m.pt. 222° (223·5°–224·5°).   The values given in brackets are those found by Petrow (*loc. cit.*).

REFERENCES.

Borsche, W., 1910. *Liebig's Ann.*, **377**, 70.
Claisen, L., and Fischer, L., 1888.   *Ber. dtsch. chem. Ges.*, **21**, 1135.
Combes, A., 1888.   *C.R. Acad. Sci. Paris*, **106**, 142.

Petrow, V. A., 1942. *J. chem. Soc.*, 693.

Roberts, E., and Turner, E. E., 1927. *J. chem. Soc.*, 1832.

Romet, M., 1935. *C.R. Acad. Sci. Paris*, **200**, 1676.

Thielpape, E., 1922. *Ber. dtsch. chem. Ges.*, **55**, 127.

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SOME REACTIONS OF AN ANGULAR PHENYL COMPOUND.

By K. H. B. Green and E. Ritchie.

Substances containing an angular methyl group are well known from both natural and synthetic sources, but angular phenyl compounds are scarcely known. Allen and van Allan (1942, 1945) showed that when dimethyl-anhydro-acetonebenzil was treated with acidic dehydrating agents it formed a bimolecular product containing an angular phenyl group. Allen, Bell, Clark and Jones (1944) prepared some naphthoquinone derivatives bearing angular phenyl groups and Boekelheide (1947) synthesized 9-phenyl decalin and 10-phenyl decahydroquinoline. However, very little is known of the reactions of such substances and since a characteristic reaction of the angular methyl group is its elimination on dehydrogenation, it was of interest to study the dehydrogenation and other reactions of an angular phenyl substance. The substance chosen was the readily accessible 11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine.

When the oily phenylhydrazone of 2-phenyl *cyclo*hexanone was refluxed with glacial acetic acid a vigorous reaction occurred and *11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine* (I) was formed in good yield together with a smaller amount of *1-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazole* (II). These substances are readily separated and distinguished from one another because I is basic and II is neutral. They were characterized by their yellow and reddish brown *picrates* respectively.

I.   II.

Barclay and Campbell (1945) have shown that tetrahydrocarbazoles, and hexahydrocarbazoles especially, are smoothly dehydrogenated by chloranil to carbazoles. When their procedure was applied to II it readily yielded *1-phenyl-carbazole* (III), but I which might be expected to split off benzene and hydrogen yielded only uncrystallizable tars under a variety of conditions. Similarly the dehydrogenation method of Perkin and Plant (1923), i.e. refluxing with sulphur in quinoline, gave only black resinous materials. Since hexahydrocarbazoles are much more readily dehydrogenated than tetrahydrocarbazoles, I was reduced by tin and hydrochloric acid to *11-phenyl-1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole* (IV) and its dehydrogenation by these methods attempted. But again only tars were formed.

III.   IV.

It has been shown (Ciamician, 1894) that when 2 : 3 : 3-trimethyl-indolenine-methiodide (V) is heated, it loses methyl iodide to form 1 : 2 : 3-trimethyl-indole. The similarly constituted *11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine-methiodide* (VI) however did not split off iodobenzene on heating, but instead gave a neutral substance, $C_{19}H_{19}N$, evidently formed by rupture of the reduced ring. It is probably *1-methyl-2-($\triangle$-3'-butenyl)-3-phenyl-indole* (VII).

V.   VI.   VII.

A few other experiments also were carried out on VI. When treated with sodium hydroxide it yielded a base which although rapidly turning purple on exposure to air could be distilled under reduced pressure. Treatment of the distilled base with hydriodic acid regenerated VI and by analogy with the behaviour of V with alkali (Brunner, 1900) it is formulated as *9-methyl-11 phenyl-2 : 3 : 4 : 11-tetrahydrocarbazole* (VIII). Support for this structure was found in the observation that oxidation by permanganate produced an acid, $C_{19}H_{19}NO_3$, which must be *1-methyl-3-phenyl-3-(3'-carboxypropyl)-oxindole* (IX)-

VIII.   IX.

EXPERIMENTAL.

11-Phenyl-1 : 2 : 3 : 4-Tetrahydrocarbazolenine (I) and 1-Phenyl-1 : 2 : 3 : 4 : Tetrahydrocarbazole (II).

When phenylhydrazine (12·8 g.) and 2-phenyl *cyclo*hexanone (20·8 g.) were warmed together on the water bath, water soon began to separate. After 20 minutes the mixture was cooled extracted with ether, the solution dried and the ether removed. The residual thick oil, which. could not be crystallized, was cyclized by refluxing it in glacial acetic acid (150 c.c.) for one hour. After diluting with water, the reaction mixture was basified and extracted with ether. The ether solution was then extracted with dilute hydrochloric acid, washed and dried.

The acid extract on basification yielded the carbazolenine (I) which after crystallization from aqueous alcohol formed colourless needles (14·5 g.) melting at 128°.

Found : C, 86·5 ; H, 7·0 ; N, 5·7%. Calculated for $C_{18}H_{17}N$: C, 87·5 ; H, 6·9 ; N, 5·7%. The *picrate* crystallized from alcohol in yellow rhombs melting with decomposition at 185°. Found : N, 11·9%. Calculated for $C_{24}H_{20}N_4O_7$: N, 11·8%.

The ether solution on evaporation gave a thick gum which could not be crystallized. However, it readily yielded a crystalline picrate, which on decomposition furnished the tetra-hydrocarbazole (II) which then crystallized from aqueous alcohol in large colourless needles (1·4 g.) which melted at 98°.

Found : C, 87·0 ; H, 6·8 ; N, 5·7%. Calculated for $C_{18}H_{17}N$: C, 87·5 ; H, 6·9 ; N, 5·7%. Its *picrate* crystallized from alcohol in dark brown needles melting at 131°. Found : N, 11·8%. Calculated for $C_{24}H_{20}N_4O_7$: N, 11·8%.

1-Phenylcarbazole (III).

A solution of chloranil (2 g.) and the tetrahydrocarbazole (II ; 1 g.) in pure dry xylene (30 c.c.) was refluxed for 24 hours. After cooling, the tetrachloroquinol was filtered off and the filtrate washed with aqueous sodium hydroxide, dried and evaporated under reduced pressure. The residue crystallized from alcohol in colourless plates (0·65 g.) melting at 139°.

Found : C, 88·4 ; H, 5·5 ; N, 5·7%. Calculated for $C_{18}H_{13}N$: C, 88·9 ; H, 5·4 ; N, 5·8%. Its *picrate* separated from alcohol in magnificent red needles melting at 153°. Found : N, 12·1%. Calculated for $C_{24}H_{16}N_4O_7$: N, 11·9%.

11-Phenyl-1 : 2 : 3 : 4 : 10 : 11-Hexahydrocarbazole (IV).

The carbazolenine (I ; 5 g.), concentrated hydrochloric acid (10 c.c.), alcohol (10 c.c.) and tin (10 g.) were refluxed on the water bath for six hours. Whilst still hot, the supernatant liquid was decanted from undissolved tin into a large excess of dilute sodium hydroxide. The product, isolated by extraction with ether, was finally crystallized from aqueous alcohol separating as colourless needles (2 g.) melting at 118°.

Found : N, 5·6%. Calculated for $C_{18}H_{19}N$: N, 5·6%. Its *picrate* crystallized from alcohol in yellow needles melting at 175°. Found : N, 11·8%. Calculated for $C_{24}H_{22}N_4O_7$: N, 11·7%.

Methiodide of I.

When a solution of the base (I ; 5 g.) in methyl-iodide (15 g.) was allowed to stand at room temperature the product (VI) gradually separated. After three hours it was collected, washed with dry ether and recrystallized from aqueous alcohol separating as pale yellow prisms (6 g.) which on heating began to decompose at about 130°.

Found : N, 3·3%. Calculated for $C_{19}H_{20}IN$: N, 3·6%.

Pyrolysis of VI.

The methiodide (VI ; 5 g.) was gently heated with a free flame at 30 m.m. until decomposition began and the pressure rose rapidly. After the reaction had subsided, and the pressure had fallen, a light amber viscous oil was distilled over. Its solution in alcohol gradually deposited VII (1 g.) which was finally obtained as slightly yellow needles melting at 107°.

Found : C, 86·7 ; H, 7·2 ; N, 5·7%. Calculated for $C_{19}H_{19}N$: C, 87·4 ; H, 7·3 ; N, 5·4%. Its *picrate* crystallized from alcohol in fine brown needles melting at 99°. Found : N, 11·8%. Calculated for $C_{25}H_{22}N_4O_7$: N, 11·4%.

Action of Sodium Hydroxide on VI.

A solution of VI (5 g.) in hot water (200 c.c.) was treated with sodium hydroxide (10 c.c. of 10%) and the mixture cooled. The product (VIII) isolated by ether, distilled at 215°/3 mm. in almost quantitative yield as a viscous colourless oil. It crystallized on rubbing with light petroleum, but since it rapidly became purple on exposure to air further purification and analysis were not attempted. When treated with hydriodic acid VI was regenerated.

Its *picrate* crystallized from alcohol in yellow needles melting at 150°. Found : N, 11·7%. Calculated for $C_{25}H_{22}N_4O_7$: N, 11·4%.

Oxidation of VIII.

A solution of potassium permanganate (1·5 g.) in water (15 c.c.) was gradually added to a boiling solution of VIII (5 g.) in acetone (15 c.c.).   Reaction was rapid and after a short time the manganese dioxide was filtered off, washed with water and the combined filtrates evaporated to a small bulk.   Acidification then precipitated IX which crystallized from aqueous alcohol in colourless needles (2·1 g.) melting at 146°.

Found : N, 4·5%.   Calculated for $C_{19}H_{19}NO_3$: N, 4·5%.

ACKNOWLEDGEMENT.

REFERENCES.

Allen, C. F. H., Bell, A., Clark, J. H., and Jones, J. E., 1944.   *J. Amer. chem. Soc.*, **66**, 1617.
Allen, C. F. H., and van Allan, J., 1942.   *J. Amer. chem. Soc.*, **64**, 1260.
———————————————————— 1945.   *J. Org. Chem.*, **10**, 333.
Barclay, B. M., and Campbell, N., 1945.   *J. chem. Soc.*, 530.
Boekelheide, V., 1947.   *J. Amer. chem. Soc.*, **69**, 790.
Brunner, K., 1900.   *S.B. Akad. Wiss. Wien.*, **109**, IIB, 24.
Ciamician, G., 1894.   *Ber. dtsch. chem. Ges.*, **27**, 3077.
Perkin, W. H., and Plant, S. G. P., 1923.   *J. chem. Soc.* 676.

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ANODIC AND CATHODIC POLARIZATION OF COPPER IN ACETIC ACID.

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With five figures.

INTRODUCTION.

In a series of papers the author (Bosworth, 1949) has described an attempt to apply the principles of dimensional analysis to metallic corrosion. From studies of the rates of corrosion under standardized conditions of forced and• natural convection it was found that five properties were concerned in determining the rate of corrosion for a given system under given external conditions. These properties were :

(a) A maximum corrosion rate (q_0) given by the rate at which corrosion would proceed were all limitations due to slow diffusion or convection made negligibly small.

(b) A conductivity term (j) equal to the rate at which the liquid acting as the corrodant would allow the controlling depolarizing agent to flow to the surface under unit driving force or potential difference for the type of flow concerned.

(c) A capacity term (K), or the change in the driving force for unit change in the concentration of the depolarizing agent produced by means of the corrosion reaction.

(d) The density change produced by unit change in the concentration of the depolarizing agent, and

(e) The driving force (E) for the corrosion reaction.

However, the experiments already described were capable of giving only four independent properties. They gave no measure of E and further gave only j and K figures in terms of the products jE and KE respectively. It thus appears desirable that some method of estimating E for the systems considered earlier be investigated.

The quantity E, if it is to be a measure of the potential for the flow of the depolarizing agent from bulk of the corrodant liquid to the metal surface, must clearly be some measure of the work done in taking unit quantity of the agent from a combined state on the metal surface, and, completely undoing all associated chemical reactions at constant temperature and pressure, take it to a free state in the bulk of the corrodant liquid. If the flow is to be measured in terms of the movement of any essential reagent concerned in the corrosion reaction the associated potential could be measured in terms of the work done (multiplied if necessary by any convenient, but constant, factor) in allowing unit quantity of the reagent concerned to be taken from metal surface to bulk liquid by a reaction which undoes the process of corrosion. Since the flow has been recorded in terms of the passage of unit mass of metal from surface to liquid, the potential is obviously a measure of the work done to send unit mass of metal back again to the surface, and this is equal to the (non-molar) Gibbs' free energy

for the particular reaction concerned. A measurement of the e.m.f. which just balances the tendency of the metal to dissolve is, at constant temperature, a constant multiple of this quantity.

The effective e.m.f. given by an electrode placed in an electrolyte with which no approximately reversible chemical change is possible is (as pointed out by Gatty and Spooner, 1938, p. 23) the net effect of two possible exchanges between the metal and the electrolyte. In one the metal is behaving anodically and supplying positive ions to the solution, and in the other it is behaving cathodically and receiving positive ions from the solution. If the two reactions when balanced electrically, as they must be when the charge on the electrode has ceased to change, are not balanced chemically, then a net reaction must take place at the surface. This net chemical reaction can always be balanced against a net electrical potential obtained by making the anodic areas more negative and thus repressing the dissolution of metallic ions, and by making the cathodic areas more positive and thus repressing the deposition of hydrogen ions. Direct measurement of the external potential difference between the anodic and cathodic areas required to repress the reaction is not possible and an indirect method must be devised. The method adopted was that of measuring, as a function of the current, the p.d. between electrodes anodically and cathodically polarized and an unpolarized electrode to which no net current flowed and which therefore came to a potential with respect to the solution determined by electrical balance of the anodic and cathodic reactions. The polarizing current used is a measure of the rate of transfer of ions from the anodic to the cathodic areas, and the polarization is a measure of the internal resistance offered to this transfer. When the rate of transfer of ions is made electrochemically equivalent to the quantity q_0 then the arithmetic sum of the overpotentials must be equal to the required driving force E. In this paper we will be concerned only with a measure of the driving force for copper in acetic acid-acetic anhydride mixtures. Other systems could be studied in a similar manner.

To convert our q_0 values into the equivalent current density terms we require a knowledge of the valence of the copper ion actively concerned in the electrode reaction. Since experiments have shown that the rate of corrosion of copper in acetic acid is increased threefold or more by the addition of small amounts of cupric ions to the solution (for example by dissolving 1% of cupric acetate in the acetic acid), it is therefore reasonable to assume that the oxidation-reduction reaction

$$Cu^{++} + Cu^{\circ} \rightarrow 2Cu^{+}$$

plays at least an important part in the anodic attack. On this basis we may write the current density (i) in amperes per sq. cm. as electrochemically equivalent to a corrosion rate of

$$5 \cdot 69 \times 10^6 \ i \ \text{mgms. dm.}^{-2} \ \text{day}^{-1}$$

So that if we find the sum of the two overpotentials when i is made equivalent to the recorded values of q_0 we have a means of deducing the driving force, or corrosion cell e.m.f.'s E.

Quite apart from this use of the experimental data to give a quantity concerned in corrosion problems in acetic acid media, the general behaviour of polarized electrodes in non-aqueous solvents is a subject which is now receiving some attention, particularly at the hands of Bockris (1947) and his collaborators.

<div align="center">EXPERIMENTAL.</div>

Since the complete curves of anodic and cathodic overpotential versus current density were required, and further since the electrolytes to be used were often of very low electrical conductivity, the commutator method was employed.

An outline of the circuit diagram is given in Figure 1. In this circuit a battery B drives a primary current through a milliammeter A, controlling resistance R, standard set of resistances (decade box) S, and triple gang commutator C_1, C_2, C_3 to the triple electrode system E_1, E_2, E_3. E_1 was the cathode, E_3 the anode, and E_2 a reference electrode. The milliammeter A was used only in setting a suitable value for the polarizing current. The value of the current was determined by measurement of the p.d. across S. During that commutator half cycle for which no primary current flowed in the electrode circuit the electrodes were connected to the triple throw, double pole switch T, the reference electrode and cathode to T_1 and the anode and reference electrode to T_2. The third pole T_3 of the switch was connected across the standard resistance S only during the half cycle for which primary current is flowing, for the other half of the cycle T_3 was an open circuit. The switch terminals lead to a potentiometer which thus could measure the polarizing current (p.d. across S), the cathodic polarization (p.d. between E_2 and E_1) or the anodic polarization (p.d. between E_3 and E_2).
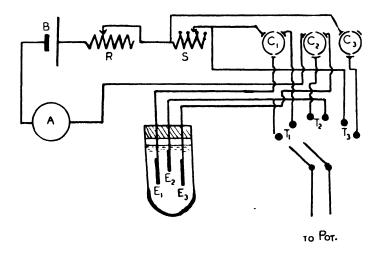
Fig. 1.

The electrodes were of copper strip $1 \cdot 25$ cm. wide and immersed 4 cm. in the electrolyte. The copper surfaces were prepared by polishing with gauge 0 emery paper followed by heating to dull redness and quenching in alcohol. The electrolytes used were 50% and 80% aqueous acetic, glacial acetic acid (95%) and acetic anhydride. In the former two electrolytes the battery B was a six-volt storage battery and in the latter two a two hundred-volt battery eliminator was used with suitable modification to the resistances.

The mechanical commutator method as here used has been regarded with suspicion when used with the more usual aqueous solutions on account of the decay of the polarization current during the " off " cycle of the commutator. Here where we are dealing with solutions of high electrolytic resistivity, low ionic concentration and high permittivity, it is to be expected that the time of discharge of the surface double layer will be large. Indeed the use of various commutator speeds from 40 to 400 r.p.m. have shown that the polarization curves in the liquid of lowest resistivity (the 50% acetic acid) are independent of the commutator speed over this range.

The Polarization Curves.

The experimental results for the current density versus anode and cathode polarizations are shown in Figure 2. The current density recorded is that for the charging half cycle only, and not the average value over the whole cycle as read by the milliammeter A. Several interesting features emerge from these graphs. In the non-aqueous solutions the anodic and cathodic polarizations are approximately equal at equal current densities (*i*). The measured polarizations are not exactly the same as normal overvoltages which are measured against a reversible reference electrode, whereas the reference electrode in the present experiments is at a non-reversible corrosion potential. Nevertheless the measured polarization (*V*) will differ only slightly in magnitude for normal anodic and cathodic overvoltages, and certainly the sum of the two polarizations will be equal to the sum of the anodic and cathodic overvoltages.

In all four cases of polarization in the non-aqueous solvents a plot of log *i* versus log *V* gave satisfactory straight lines. These lines are shown in Figure 3. From the slopes of these lines we may calculate factors α defined as

$$\alpha = 2 \cdot 303 \frac{RT}{F} \frac{d \log i}{d \log V} \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

The factors α and the quantities i_0 (the antilogs of the intercepts) calculated from the curves shown in Fig. 3 are given in Table 1.
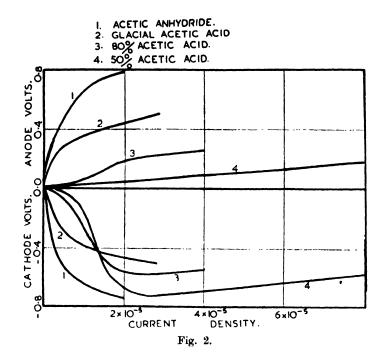
TABLE I.

Polarization of Copper at 27° C.
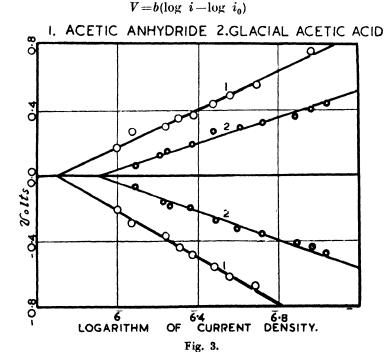
Electrolyte Used.	Anodic Polarization.		Cathodic Polarization.	
	i_0 in amps. cms.$^{-2}$.	α	i_0 in amps. cms.$^{-2}$.	α
Glacial acetic acid	$7 \cdot 1 \times 10^{-7}$	$0 \cdot 184$	$7 \cdot 6 \times 10^{-7}$	$0 \cdot 168$
Acetic anhydride	$4 \cdot 5 \times 10^{-7}$	$0 \cdot 127$	$4 \cdot 5 \times 10^{-7}$	$0 \cdot 102$

Collected data on the two factors i_0 and α have been given by Bowden and Agar (1938). For cathodically polarized copper in aqueous mineral acids i_0 ranges from 10^{-5} to 10^{-6} and α from $0 \cdot 8$ to $0 \cdot 5$. Similar values of α have been recorded for oxygen overvoltages (Bowden, 1929), while smaller values of the order $0 \cdot 25$ were recorded by Bowden and Kenyon (1935) for hydrogen overvoltages in alkali solutions. Since α measures the rate of variation of the activation energy for deposition of ions with the external field, it has been concluded that the mechanism for deposition of hydrogen (cathodic overvoltage) is different in alkaline solution from that in (aqueous) acids. The figures recorded above for the non-aqueous conductors examined indicate still lower values for α and thus still less dependence of the activation energy for the deposition of ions on the external field.

In the more nearly aqueous solutions the curves of Fig. 2 show an anodic polarization much less than the cathodic. In the 50% solution the cathodic polarization remains quite small until a current density of the order 10^{-5} amp. cms.$^{-2}$ is reached when the polarization increases rapidly with further increase in the current density obtaining a maximum value of $0 \cdot 74$ volt and thereafter *decreasing* with further increase in the current density in such a way that the sum of the two polarizations remains constant and equal to $0 \cdot 79$ volt. The

1. ACETIC ANHYDRIDE.
2. GLACIAL ACETIC ACID
3. 80% ACETIC ACID.
4. 50% ACETIC ACID.

Fig. 2.

behaviour of the 80% solution is in a way intermediate between that of the 50% and the 95% solution, showing a less abrupt rise in the cathodic polarization and intermediate values for the anodic polarization. Detailed examination of the polarization curves show that neither of these solutions follow the exponential law

$$V = b(\log i - \log i_0)$$

1. ACETIC ANHYDRIDE 2. GLACIAL ACETIC ACID

Fig. 3.

even approximately over any appreciable range.   It is accordingly impossible to derive values of α or i_0 for these systems.

The data as given in Figure 2 refer to unstirred solutions initially saturated with air.   Solutions prepared by boiling and cooling in a stream of hydrogen gave substantially the same curves.   The act of stirring the electrolyte had but little effect on the anodic overpotential, but produced a very severe reduction of the cathodic overpotential in the region of current density in which the overpotential is rapidly rising.   After a change in current density the overpotential generally settled down within a minute or two to the final new value.   Again, however, in the case of the cathode in the region of rapidly changing overpotential the value at any fixed current density increased with time over a longer period and approached the final value only after about 20 minutes.   The depression produced by stirring was again only of a temporary nature and the original value was restored on standing.
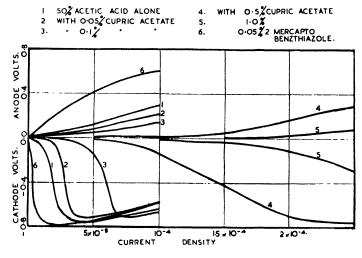
Fig. 4.

There was, however, a limit to which the effect of slow changes could be studied in these systems.   On standing the copper electrodes slowly dissolved in the acetic acid, and since the presence of copper acetate in solution profoundly modified the nature of the polarization curves it was necessary to change the acid at fairly frequent intervals, particularly when dealing with high current densities.   The effect of cupric ions on the polarization curves in 50% acetic acid is shown in Figure 4, where the polarization curves are given for systems with various quantities of cupric acetate added.   At any fixed current density the addition of cupric acetate lowers both anodic and cathodic overpotential and also moves the point of rising cathodic overpotential into progressively higher and higher current densities.   Cupric acetate is a corrosion accelerator in this system.

The opposite effect is shown by mercapto-benzthiazole, a corrosion inhibitor for copper.   The addition of 0·05% of this substance both raises the overpotential and shifts the region of rapidly changing cathodic overpotential to lower current densities.   A polarization curve for copper in 50% aqueous acetic acid with the addition of 0·05% of 2-mercaptobenzthiazole·is also shown in Figure 4.

So far no chemical interpretation of the anodic and cathodic reactions concerned in the polarization observed in these liquids has been attempted. All the anodic polarization curves and the cathodic curves for glacial acetic acid and for acetic anhydride follow, as has already been indicated, a Tafel equation. However, the form of the cathodic polarization curves for the 50% and 80% aqueous acetic acid resembles that of a polarographic curve and strongly suggests that a change in the mechanism of the transport of the electrical charge occurs over a comparatively narrow range of current densities, the change involving the replacement of ions of comparatively low overvoltage by those of higher overvoltage as effective carriers to the cathode surface. Such a change, for example, might consist in the replacement of copper ions, originating from copper dissolved at the anode, by hydrogen ions when the current density becomes too heavy for transport by the attenuated array of copper ions. If this interpretation is correct a linear relationship is to be expected between the concentration of copper ions and the current density at which the change in the nature of the cathodic reaction occurs. Figure 5 shows the concentration of
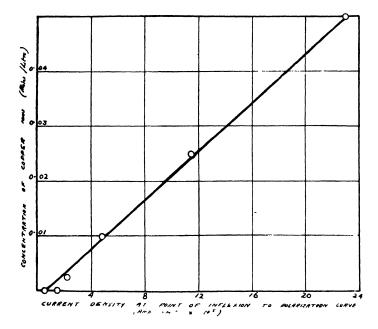
Fig. 5.

cupric ions Cc_u^{++} plotted against the current density i_{crit} required to give the point of inflexion on the cathodic polarization curve. The data used were those obtained from Figure 4. Figure 5 shows a linear relationship between Cc_u^{++} and i_{crit}. The extreme left-hand point on the figure refers to the solution of 2-mercaptobenzthiazole and an interpretation of the effect of this substance on the cathodic polarization curves now becomes clear. 2-Mercaptobenzthiazole forms a stable complex with cupric ions and thus reduces the current density which may be carried by these ions.

From the slope of the line shown in Figure 5 it will be seen that

$$\frac{d\ i_{crit}}{d\ Cc_u^{++}} = 4 \cdot 5 \text{ amps. cms. moles}^{-1}.$$

Now it may readily be shown by solution of the Fick diffusion equation (see for example Kolthoff and Lingane, 1941, p. 435) that the limiting diffusion current is given by

$$\frac{d \ i_{crit}}{d \ C} = \frac{D}{\delta} z \mathbf{F},$$

where D is the diffusion coefficient for the ions deposited,

  δ is the thickness of the diffusion layer at the electrode,

  z is the valence of the ions ($z=2$ for cupric ions), and

  $\mathbf{F}$ is the Faraday.

The diffusion coefficient for copper ions in dilute aqueous solution is given (Kolthoff and Lingane, p. 45) as $7 \cdot 2 \times 10^{-6}$ cms.^{2} secs.$^{-1}$. It is not expected that the value would be very different in dilute solution in acetic acid. Frenkel (1946) has remarked on the striking constancy of the diffusion coefficients in different liquid solvents. Accordingly we may use the equation above to derive an approximate value for the effective diffusion layer thickness (δ), namely

$$\delta = 0 \cdot 3 \text{ cm.}$$

which may be compared with the figure of $0 \cdot 03$ cm. quoted by Glasstone (1941) as a typical diffusion layer thickness for unstirred solutions at room temperatures. The deduction thus appears to lend considerable support to the suggestion that the lower part of the cathodic polarization curves is associated with the discharge of cupric ions.

 The upper part of the polarization curves in these same solutions is presumably due to hydrogen deposition. Here also no equation of the Tafel form appears to be applicable. Indeed the measured overvoltage in all cases drops with further increase in the current density, suggesting, on taking the observations at their face value, that the hydrogen film formed at the higher current densities is electro-negative in character, similar, for example, to the hydrogen films formed on tungsten *in vacuo* (Bosworth, 1937).

 However this apparent drop in the cathodic overvoltage may or may not be real. The commutator method of investigation used in this work is known to give low figures at high current densities (Ferguson, 1947). Use of the direct method of measurement in this work was excluded on account of the high resistivity of the liquids under test. In some cases the total p.d. between anode and cathode (net polarization plus ohmic drop in solution) was over 200 volts during the charging half of the commutator cycle, while the total measured polarization during the open half of the commutator cycle was less than one volt. The time constant for the decay of the overvoltage film is equal to the product of the resistance and the capacity, both measured per unit area of electrode surface. Bowden and Grew (1947) have found an electrostatic capacity (for a mercury-sulphuric acid interface) of 20 μF cm.$^{-2}$ and other workers have reported figures of a similar order of magnitude. As mentioned above, the resistivities of the liquids used in this work were abnormally high, ranging from 40,000 to 10,000,000 ohms per square centimetre of the electrode surface. It is thus to be expected that the time constants for the decay of the overvoltage films would be of the order $0 \cdot 8$ to 200 seconds. Since the commutator remained in the " open " condition for only $0 \cdot 2$ secs., it is not to be expected that errors due to rapid decay would be appreciable except, possibly, in the more highly conducting liquids (50% aqueous acetic acid with copper acetate in solution) and at the highest current densities, and it is only here that difficulties in the interpretation of the results were experienced.

The Corrosion Cell E.M.F.'s.

The corrosion cell e.m.f.'s for copper in these liquids may be derived from the curves shown in Figure 2. Data were first obtained for the rate of corrosion of copper specimens, from the same batch as the electrodes, at 27° C. and in acetic anhydride, acetic acid and 50% aqueous acetic acid. The test surfaces consisted of plane faces surrounded by a " guard ring " of the same metal, held horizontal and immersed at different depths (z) below the free surface of the corrodant. The rate of dissolution q of the face (in milligrammes per square decimetre per day) was measured as a function of z and by extrapolation to zero z a corrosion rate q_0 is found which is assumed to be the rate when there is no limitation of the chemical attack due to slowness of the diffusion to or from the surface. Details of these measurements have already been given (Bosworth, 1949). The values of q_0 are then converted into equivalent current densities. The sum of the overvoltages at these current densities was then read off from Figure 2 and this sum was taken as a measure of the corrosion cell e.m.f. The results thus obtained are given in Table II. It will be noted in particular

TABLE II.

Maximum Corrosion Rates and Cell E.M.F.'s for Copper.

Electrolyte.	q_0.	Equivalent Current Density.		Cell E.M.F.
Acetic anhydride	51	$9 \cdot 0 \times 10^{-6}$ amps. cms.$^{-2}$		$1 \cdot 30$ volts
Glacial acetic acid	100	$17 \cdot 7 \times 10^{-6}$,,	,,	$1 \cdot 00$,,
50% acetic acid	97	$17 \cdot 1 \times 10^{-6}$,,	,,	$0 \cdot 70$,.

that the value for q_0 in 50% acetic acid is beyond the inflexion of the cathodic polarization curve. This must clearly be so as the deposition of cupric ions cannot be the cathodic reaction in the corrosion of copper.

SUMMARY.

The cathodic and anodic overpotentials of copper in 50% and 80% aqueous acetic acid, in glacial acetic acid and in acetic anhydride have been measured as a function of the current density by the commutator method, it having been shown that the time constants in these poorly conducting media are long.

The two non-aqueous liquids gave polarization curves of the logarithmic

type. The dimensionless factors $\alpha \left(2 \cdot 303 \frac{RT}{F} \cdot \frac{d \log i}{dV} \right)$ calculated from the slopes

are only of the order $0 \cdot 10$ to $0 \cdot 18$, the anodic value being slightly lower than the cathodic. These low figures indicate that the activation energy for the deposition of ions in these solvents are much less effected by external fields than in aqueous solutions.

In 50% aqueous acetic acid the cathodic overpotential shows a sudden rise over a narrow range of current densities. The current density at which this rise occurs is directly proportional to the concentration of cupric ions present in the acetic acid solution. The addition of 2-mercaptobenzthiazole which lowers the concentration of free cupric ions produces a high cathodic polarization at very low current densities and incidentally is a very effective corrosion inhibitor.

Corrosion cell e.m.f.'s have been deduced from a combination of the over-voltage curves with independently measured corrosion rates. These e.m.f.'s

are : 1·3 volts, copper in acetic anhydride ; 1·0 volts, copper in glacial acetic acid ; and 0·7 volt, copper in 50% aqueous acetic acid.

REFERENCES.

Agar, J. N., and Bowden, F. P., 1938. *Ann. Rep. Chem. Soc.*, **35**, 90-113.

Bockris, J. O'M., 1947. *Faraday Soc. Discussion*, **1**, 95-106, 229-235 ; *Nature*, **159**, 401-402.

Bosworth, R. C. L., 1937. *Camb. Phil. Soc. Proc.*, **33**, 394-402.

———————————— 1949. THIS JOURNAL,   .

Bowden, F. P., 1929. *Proc. Roy. Soc.*, **126A**, 107-125.

Bowden, F. P., and Grew, K. E. W., 1947. *Faraday Soc. Discussions*, **1**, 91-94.

Bowden, F. P., and Kenyon, H. F., 1935. *Nature*, **135**, 105.

Ferguson, A. L., 1947. *Faraday Soc. Discussions*, **1**, 50-57.

Frenkel, J., 1946. " Kinetic Theory of Liquids." Oxford.

Gatty, O., and Spooner, E. C. R., 1938. " The Electrode Potential Behaviour of Corroding Metals in Aqueous Solution." Oxford.

Glasstone, S., 1946. " Textbook of Physical Chemistry." Van Nostrand, N.Y.

Kolthoff, I. M., and Lingane, J. J., 1941. " Polarography." Interscience Publishers, New York.

THE CHEMISTRY OF RUTHENIUM.

PART III. THE REDOX POTENTIALS OF THE RUTHENIUM II COMPLEXES WITH SUBSTITUTED DERIVATIVES OF 2 : 2′ DIPYRIDYL AND o-PHENANTHROLINE.

By F. P. DWYER, D.Sc.

In a previous paper (Dwyer, Humpoletz and Nyholm, 1946) the preparation of the tris o-phenanthroline ruthenium II salts was described, and the potential of the reaction $Ru(phenan)_3^{+++} - e' \rightarrow Ru(phenan)_3^{+++}$ was determined. The potential was found to decrease with increasing acid concentration, and was notably unstable except in concentrated acid solution. The instability was undoubtedly due to auto-reduction of the oxidant ion, since the blue solution of the oxidised material became orange red—the colour of the original ruthenium II compound—on standing for a short time. It thus appeared that phenanthroline itself, whether freed by dissociation or bound to the ruthenium, was capable of being oxidised at the high potentials operating in the weakly acid solutions. The potential of the system in 0·1 normal acid, 1·29 volts, was lower than that found for the corresponding 2 : 2′ dipyridyl compound (Steigman, Birnbaum and Edmonds, 1942), although by analogy with the ferrous compounds (Dwyer and McKenzie, 1947) the phenanthroline complex was expected to have the higher value.

With small samples of various substituted derivatives of 2 : 2′ dipyridyl and o-phenanthroline, made available by Dr. A. Albert, a further study has been made of the ruthenium compounds, and at the same time the potentials of the 2 : 2′ dipyridyl and o-phenanthroline complexes themselves have been determined by a more reliable procedure. Although the evaluation of redox potentials by the titrimetric method does not give highly accurate results (Dwyer, Nyholm and McKenzie, 1944), the instability of the oxidised form of most of the ruthenium complexes precludes the standard procedure of allowing an electrode to come to equilibrium in an equimolar mixture of the pure oxidant and reductant, and hence some titrimetric procedure must be used. The most reliable of such methods due to Smith and Richter (1944) involves the use of an accurately standardised solution of the reductant, to which is added sufficient of the oxidising agent to convert exactly one-half to the oxidised form. The oxidising agent is selected so that its potential is at least 0·2 to 0·3 volt higher than the redox potential of the substance under examination. The potential of a suitable electrode in such a mixture is found to rise rapidly to a maximum, which persists for a variable time depending on the stability of the oxidised form. The maximum potential represents the most probable value of the true redox potential. In the present study this method has been used for the ruthenium II complexes with 2 : 2′ dipyridyl and o-phenanthroline, but with the substituted derivatives which were available in only small amounts the usual titrimetric method was used.

It has been found that, over a wide range of acidities, the complex with o-phenanthroline had always a slightly higher potential than the 2 : 2′ dipyridyl complex. The substituted derivatives followed the same trend with ruthenium

as with ferrous iron (Smith and Richter, *loc. cit.*). Thus the presence of methyl substituents, which raise the basicity of the chelate group, lowered the potential ; whilst bromo substituents which have the opposite effect on the basicity, raised the potential. The presence of methyl substituents in both the parent bases lowered the stability of the oxidised form of the complex, probably by oxidation of such groups. The complex derived from 5-bromo o-phenanthroline, which had the extremely high redox potential of 1·41 volts, was the most unstable of all in the oxidised form. In this compound it is possible that the phenanthroline ring is attacked at the high potential.

EXPERIMENTAL.

Ruthenium II Complexes. These were prepared in a similar manner to the tris-o-phenanthroline compound, described previously (*loc. cit.*) by refluxing an aqueous solution of potassium pentachloro-hydroxy ruthenate IV (1 mol.), with the base (3 mols.), until a greenish brown solution resulted, and then adding a few drops of 30% hypophosphorous acid just neutralised with caustic soda. The heating was continued until the colour had changed to deep orange red, when the mixture was filtered, and potassium iodide added. The compounds then crystallised in orange to orange-red needles or prisms. They were recrystallised from hot water, and dried over concentrated sulphuric acid. The bases used were 2 : 2'-dipyridyl, 4 : 4'-dimethyl-dipyridyl, 5 : 5'-dimethyl-dipyridyl, 5-methyl-o-phenanthroline, 5-bromo-o-phenanthroline and 5-nitro-o-phenanthroline. Tris-5-bromo-o-phenanthroline ruthenium II iodide could not be obtained pure, presumably owing to reduction of the nitro group by the sodium hypophosphite. Under the conditions of drying employed, the compounds derived from 2 : 2'-dipyridyl and its substituted derivatives were the pentahydrates, whilst those derived from o-phenanthroline were tetrahydrates.

TABLE I.

Ruthenium Compounds : $RuB_3.I_2.4$ or $5H_2O$.

Base.	M.P.	Calculated.			Found.		
		C.	H.	N.	C.	H.	N.
2 : 2' dipyridyl	71°	39·4	3·45	8·98	39·3	3·4	9·1
4 : 4' (CH₃)₂ dipy. ..	169°	43·28	4·59	8·42	43·4	4·3	8·5
5 : 5' (CH₃)₂ dipy. ..	114°	43·28	4·59	8·42	43·2	4·7	8·6
5-CH₃-o-phen.	112°	46·35	3·75	8·32	46·4	3·5	8·3
5-bromo-o-phen... ..	117°	35·85	2·40	6·97	35·7	2·3	7·2

The iodides were transformed to the more soluble nitrates by dissolving in a small amount of hot water and adding a slight excess of silver nitrate. The mixture was evaporated to dryness to coagulate the silver iodide and to prevent the formation of complexes of the type $Ru(phenan)_3(AgI_2)_2$. The mass was then extracted with water, the silver iodide filtered out, and the solution made up to M/200. The nitrates and sulphates of the complexes with 5-bromo and 5-methyl-o-phenanthroline were so sparingly soluble that the solution were made M/400.

Apparatus and Procedure. The redox apparatus consisted of a small beaker, fitted with a stopper, carrying a platinum foil electrode, an ammonium nitrate salt bridge, tubes for the ingress and outlet of carbon dioxide, and a micro burette. The potential of the saturated calomel electrode at 15° C. was taken as 0·2500 volt.

The complex ruthenium compound (5 c.c.) was mixed with distilled water, and nitric acid and the total volume made up to 14 c.c. Since the amount of oxidising agent required for half oxidisation was $1\cdot0$ to $1\cdot2$ c.c., the concentration of ruthenium solution at the equimolar point was M/600, except with the 5-bromo and 5-methyl-o-phenanthroline compounds, when it was M/1200. The mixture was stirred with a rapid stream of purified carbon dioxide, and cooled to $0°$ C. in an ice bath. The oxidising solution of ceric nitrate was $0\cdot02$ N approximately, in nitric acid of the same concentration as the ruthenium complex. It was standardised each time immediately before addition to the ruthenium solution, using a fresh solution of ferrous ammonium sulphate as the standard.

The determination of the redox potentials of the $2:2'$ dipyridyl and o-phenanthroline compounds was made by adding the calculated volume of the oxidising agent for half oxidisation as rapidly as possible, and immediately reading the potential on the platinum electrode. The potentials rose rapidly during the first one to two minutes and then remained stationary for a varying time before falling. The highest potential was taken as the redox potential. The potentials of the substituted compounds were obtained by rapid titration until (approximately) the substance was half oxidised, when it was done more slowly, accepting the highest value, and then rapidly to the end point. From the end point titration, the point of half oxidisation was calculated in the usual way. Except with the $2:2'$ dipyridyl compound, which was the most stable, the potentials are not considered more accurate than $+5$mv. The results are shown in Table II.

<div align="center">TABLE II.</div>

The Redox Potentials of the Ruthenium II Complexes with Substituted Derivatives of $2:2'$ Dipyridyl and o-Phenanthroline in Nitric Acid.

Acid Concentration Normality.	E_h.					
	$2:2'$ dipy. Volts.	Phenan. Volts.	$4:4'$ $(CH_3)_2$ Dipy. Volts.	$5:5'$ $(CH_3)_2$ Dipy. Volts.	5-(CH_3) Phenan. Volts.	5-Br Phenan. Volts.
0·002	1·303	1·31	1·152	1·240	1·29	1·41
0·1	1·288	1·30	1·115	1·208	1·28	1·36
0·3	1·279	1·29	1·096	1·185	—	—
0·5	1·270	1·28	1·087	1·171	—	—
1·0	1·257	1·26	1·070	1·154	—	—
2·0	1·240	1·24	—	—	—	—
3·0	1·222	1·22	—	—	—	—
5·0	—	1·19	—	—	—	—

SUMMARY.

The redox potentials of the ruthenium II complexes with substituted derivatives of $2:2'$ dipyridyl and o-phenanthroline have been determined, and a redetermination of the potentials of the complexes with the parent bases have been made. Methyl groups in both bases depress the potential, whilst the potential of the complex with 5-bromo-o-phenanthroline is the highest of all. The ruthenium compounds thus follow the same trend as the ferrous compounds. At equivalent acid concentrations, the redox potentials of tris-o-phenanthroline ruthenium salts is always higher than of the tris-$2:2'$ dipyridyl analogues.

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REFERENCES.

Dwyer, McKenzie and Nyholm, 1944. THIS JOURNAL, **78**, 260.
Dwyer, Humpoletz and Nyholm, 1946. *Ibid.*, **80**, 212.
Dwyer and McKenzie, 1947. *Ibid.*, **81**, 93.
Smith and Richter, 1944. *Ind. Eng. Chem. Anal. Ed.*, **16**, 580.
Steigman, Birnbaum and Edmonds, 1942. *Ibid.*, **14**, 30.

THE CHEMISTRY OF RUTHENIUM.

Part IV. The Potential of the Quadrivalent/Trivalent Ruthenium Couple in Hydrochloric and Hydrobromic Acids.

By J. R. BACKHOUSE, M.Sc.,
and F. P. DWYER, D.Sc.

Grube and Fromm (1941) investigated the potential of the quadrivalent/ trivalent ruthenium couple in a limited range of hydrochloric acid concentrations, and found that it varied from $0 \cdot 858$ volt in 2 normal acid to $0 \cdot 908$ volt in $0 \cdot 5$ normal acid. It was concluded that the reaction was not the simple $Ru^{4+} + e' \rightarrow Ru^{3+}$; but hydrogen and chloride ions were also involved. A study of the quadrivalent/trivalent osmium couple in hydrobromic acid (Dwyer, McKenzie and Nyholm, 1946) and in hydrochloric acid (Dwyer, Humpoletz and Nyholm, 1947a) showed that whilst the potentials in hydrobromic acid were usually much lower, when the acid concentrations became small, they coincided. From this observation and the shapes of the curves it was concluded that the reaction measured in low acid concentrations was $OsO^{++} + e' \rightarrow OsO^{+}$.

The quadrivalent/trivalent ruthenium couple has now been investigated over a wide range of acid concentrations of hydrochloric and hydrobromic acids in order to determine whether a similar reaction might not apply.

As with quadrivalent osmium, simple salts of quadrivalent ruthenium do not exist. The complex hexahalogenates R_2RuX_6 ($X = Cl$, Br), the analogues of the osmium complexes used, are decomposed even in strongly acid solutions, and the hydroxypentahalogenates, $R_2(RuX_5.OH)$ result. It is probable that in very dilute acid further replacement of the halogen by hydroxyl may result, but definite compounds have not been isolated.

Trivalent ruthenium is normally obtained by treatment of the quadrivalent compounds with alcohol, sulphurous acid, or stannous chloride, or by cathodic reduction. The present authors have found silver wool especially satisfactory, as the silver halide is precipitated and easily removed.

$$(RuCl_5.OH)'' + Ag^+ + HCl \longrightarrow (RuCl_5.H_2O)' + AgCl.$$

Two series of complex salts result, $R.(RuCl_4.2H_2O)$, of which the free acid $H.(RuCl_4.2H_2O)$ has been isolated in green *cis* and red *trans* forms (Charonnat, 1931), and the pentahalogenoaquo complexes, $R_2(RuCl_5.H_2O)$ (Charonnat, *loc. cit.* ; Howe, 1927). In both compounds the molecules of water are firmly bound, whilst Buividate (1935), operating with the ammonium salt of the red series, found that excess of silver nitrate would precipitate only three of the four halogen atoms. The reaction involved was probably

$$(RuCl_4.2H_2O)' + 3Ag^+ + 3H_2O \longrightarrow (RuCl.5H_2O)^{++} + 3AgCl.$$

However, Grube and Nann (1939), by evaporating a solution of ruthenium trichloride over concentrated sulphuric acid in high vacuum, or in a current of dry hydrochloric acid at high temperatures isolated the monohydrate, $RuCl_3.H_2O$, which they concluded demonstrated the tetracovalency of ruthenium III. It was suggested that when solutions of this substance in dilute hydrochloric acid

were allowed to stand successive additions of aquo groups took place according to the scheme

$$(RuCl_3.H_2O)° \rightarrow (RuCl_2.2H_2O).Cl \rightarrow (RuCl.3H_2O).Cl_2 \rightarrow (Ru.4H_2O).Cl_3.$$

From conductivity experiments and titration with silver nitrate it was found that the first compound contained no ionisable halogen, but on standing not much more than one chlorine atom was ionised, so that the last stage of the scheme is very doubtful. It is difficult to reconcile the conflicting data of Buividate and Grube and Nann on this point, but it may be concluded that at least one chlorine atom is non-ionisable in ruthenium trichloride, and very probably two, since Buividate used an excess of silver nitrate.

Grube and Fromm (1940) also claimed the existence of the diaquo compound above in *cis* and *trans* forms. This claim was made on the observation that greenish solutions of the compound on standing became brown without any increase in the conductivity or precipitatable halogen. There is a multitude of evidence, however, for the preferred hexacovalency of trivalent ruthenium (Charonnat, *loc. cit.*; Morgan and Burstall, 1936; Werner and Smirnoff, 1920; Dwyer, Humpoletz and Nyholm, 1947*b*), and these various aquo salts, if they exist, should thus be formulated as are the aquo chromium III chlorides. The alleged green isomer is thus the *cis* form of the octahedral complex $[RuCl_2.4H_2O]^+$, or alternatively due to traces of blue ruthenium II salts obtained by carrying the reduction too far.

In this study, the oxidising solution of the hydroxypentahalogeno ruthenate IV was made up to a specified volume by the addition of acid or various salts, and distilled water and freed from oxygen by the passage of carbon dioxide. The reductant solution was made from a fresh portion of the oxygen-free oxidant solution by reduction with silver wool in an atmosphere of carbon dioxide. After mixing, the equimolar solution of oxidiser and reducer was allowed to reach equilibrium among the various ions for two weeks. During this period the potential usually fell slightly, indicating that oxidation of the ruthenium III had not occurred. The potential was measured with two independent electrodes of gold and smooth platinum, which at equilibrium gave the same potential within 0.2 millivolt. The system was badly " poised ", and measurement with the ordinary potentiometer was not possible ; but with a valve potentiometer steady reproduceable potentials were obtained.

In the presence of hydrochloric acid the potential of the system (using potassium pentachlorohydroxy ruthenate IV as the oxidant) rose rapidly, reaching a maximum at about 0.3 N acid and then decreased sharply (Table I, Curve I). The initial sharp rise in the potential can be ascribed to the reversal of the hydrolysis of the oxidant ion, since the addition of neutral salts such as ammonium sulphate to the weakly acid solution precipitated the colloidal black ruthenium dioxide. The subsequent decrease in the potential leads to the conclusion that the ionic species present in the dilute acid are chiefly cations which are gradually transformed into complex ions.

In the presence of hydrobromic acid (using potassium pentabromohydroxy ruthenate IV as the oxidant), the potential showed also a sharp rise, followed by a marked decrease. However, the potential was always much lower than in the chloride system (Table II, Curve II). It can be concluded, therefore, that unlike the osmium III/osmium IV system, different ionic species exist in the two acids, and that halogen is bound to the metal. The lower potential in hydrobromic acid is consistent with the more pronounced covalent bonding of the bromine atom.

Conclusive evidence for the pronounced effect of the halogen ion on the potential in the chloride system was obtained by a series of measurements, in which the effects of hydrogen ion, chloride ion and ionic strength were studied

TABLE I.

The Effect of Hydrochloric Acid on the Ru^{IV}/Ru^{III} Potential.
(Cf. Curve I, Fig. 1.)

Acid Concentration. Normality.	E, Observed. (Volt.)	E_h. (Volt.)
0·2	0·674	0·918
0·25	0·688	0·932
0·325	0·678	0·922
0·423	0·675	0·919
0·596	0·661	0·905
0·77	0·649	0·893
0·94	0·637	0·881
1·46	0·608	0·852
2·5	0·557	0·801
3·53	0·520	0·764
4·57	0·490	0·734
5·47	0·470	0·714

TABLE II.

The Effect of Hydrobromic Acid on the Ru^{IV}/Ru^{III} Potential.
(Cf. Curve II, Fig. 1.)

Acid Concentration. Normality.	E, Observed. (Volt.)	E_h. (Volt.)
0·2	0·491	0·735
0·25	0·531	0·775
0·472	0·503	0·747
0·916	0·480	0·724
2·03	0·436	0·680
3·58	0·395	0·639
4·25	0·380	0·624
6·02	0·357	0·601
6·91	0·340	0·584

separately. With fixed chloride ion concentrations of 0·025 N and 1·115 N the hydrogen ion concentration was increased by means of sulphuric acid (Tables III, IV, Curves III, IV). In each series the potential decreased with increasing hydrogen ion concentration, but the decrease was much smaller than with hydrochloric acid. When the hydrogen ion concentration was kept constant at 0·25 N and 1·115 N in the next series of measurements and the chloride ion concentration increased with potassium chloride, the potential decreased sharply, the curves being only slightly higher than the hydrochloric acid curve (Tables V, VI, Curves V, VI). The increase in ionic strength was made at fixed hydrogen and chloride ion concentrations by the addition of ammonium sulphate. The decrease in the potential was relatively small (Table VII).

The decrease in the potential of a redox system by the addition of neutral salts can usually be ascribed either to the disproportionate reduction of the activity of the oxidiser, by reason of its greater charge in cationic systems (such as the ferric/ferrous system), or to complex ion formation with the oxidiser. In an anionic system involving complex metallic ions, the reductant usually carries the greater charge as in the ferricyanide/ferrocyanide system (Kolthoff

TABLE III.

The Effect of Hydrogen Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Chloride Ion Concentration, 0·25 N.
(Cf. Fig. 2, Curve III.)

Total Hydrogen Ion Concentration Normality.	E, Observed. (Volt.)	E_h. (Volt.)
0·25	0·688	0·932
0·505	0·701	0·945
0·76	0·699	0·943
1·015	0·699	0·943
1·52	0·693	0·937
2·54	0·680	0·924
3·65	0·671	0·915
4·36	0·660	0·904
6·63	0·612	0·856

TABLE IV.

The Effect of Hydrogen Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Chloride Ion Concentration, ⁻·⁻⁻5 N.
(Cf. Fig. 2, Curve IV.)

Total Hydrogen Ion Concentration Normality.	E, Observed. (Volt.)	E_h. (Volt.)
1·115	0·629	0·873
2·135	0·617	0·861
3·155	0·602	0·846
4·17	0·584	0·838
6·22	0·557	0·803

TABLE V.

The Effect of Chloride Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Hydrogen Ion Concentration, 0·25 N.
(Cf. Fig. 2, Curve V.)

Total Chloride Ion Concentration, Normality.	E, Observed. (Volt.)	E_h. (Volt.)
0·25	0·688	0·932
0·425	0·695	0·939
0·687	0·671	0·915
1·125	0·646	0·890
1·65	0·620	0·864
2·26	0·598	0·842

and Tomsicek, 1935) and the chloriridate/chlororidite and bromiridate/bromiridite systems (Dwyer, McKenzie and Nyholm, 1944, 1947c). As a result, the potential rises with increasing ionic strength. It is evident that in determining the constitution of a redox system the effects of both complex ion formation and the ionic strength must be considered.

TABLE VI.

The Effect of Chloride Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Hydrogen Ion Concentration, $1 \cdot 115$ N.
(*Cf.* Fig. 2, Curve VI.)

Total Chloride Ion Concentration, Normality.	E, Observed. (Volt.)	E_h. (Volt.)
$1 \cdot 115$	$0 \cdot 629$	$0 \cdot 873$
$1 \cdot 64$	$0 \cdot 602$	$0 \cdot 846$
$2 \cdot 17$	$0 \cdot 580$	$0 \cdot 824$
$3 \cdot 13$	$0 \cdot 556$	$0 \cdot 800$

TABLE VII.

The Effect of Ammonium Sulphate on the Ru^{IV}/Ru^{III} Potential.

Hydrochloric Acid Concentration Normality.	E_h. (Volt.)	Total Normality with Ammonium Sulphate.	E_h. (Volt.)
$0 \cdot 77$	$0 \cdot 893$	$1 \cdot 27$	$0 \cdot 889$
$0 \cdot 94$	$0 \cdot 881$	$2 \cdot 45$	$0 \cdot 869$
$1 \cdot 46$	$0 \cdot 852$	$3 \cdot 98$	$0 \cdot 839$

It can be assumed from general principles that the reductant is the more cationic, and from the observations of Buividate and Grube and Nann (*loc. cit.*) it is probable that the ion present in dilute solution is the hydrated $(RuX_2)^+$ or less, probably $(RuX)^{++}$. With increasing halogen ion concentration there will be a tendency for the formation of complex anions such as $(RuX_4.2H_2O)'$ and $(RuX_5.H_2O)''$, but the stability of such ions, if the usual rule is followed, will be much smaller than similar complex anions formed by the oxidant, and their effect can thus be neglected. The separation of black ruthenium dioxide from solutions of potassium pentachlorohydroxy ruthenate IV in very dilute acid leads to the conclusion that this salt can undergo progressive dissociation. Observations on the colour of solutions of the bromo compound in various concentrations of hydrobromic acid supports this view. Thus the deep purple colour in normal hydrobromic acid gradually becomes lighter and brownish in colour-like dilute solutions of the chloro compound—as the acid is diluted and finally darkens with the separation of ruthenium dioxide. If the acid concentration is raised above $3 \cdot 5$ normal, the purple colour changes to brown, suggesting the replacement of the hydroxyl group by bromine has occurred.

$$(RuBr_5OH)'' + HBr \rightarrow (RuBr_6)'' + H_2O$$

This latter reaction cannot be performed on the chloro compound with even concentrated hydrochloric acid.

The progressive dissociation of the chloro compound can be expected to follow a scheme such as

$$(RuCl_5OH)'' \rightarrow (RuCl_4.OH.H_2O)' \rightarrow (RuCl_3.OH.2H_2O)^\circ$$
$$\downarrow$$
$$(RuCl_2.OH.3H_2O)^+ \rightarrow (RuCl.OH.4H_2O)^{++}$$
$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$
$$(RuCl.(OH)_2.3H_2O)^+ \longrightarrow RuO_2$$

The dissociation of the initial compound can be repressed by direct replacement of aquo and hydroxyl groups by chloride ions, the latter replacement being facilitated by hydrogen ions.

$$(RuCl.(OH)_2.3H_2O)^+ + 4Cl' \longrightarrow (RuCl_5.OH)'' + OH' + 3H_2O$$

$$(RuCl.(OH)_2.3H_2O)^+ + H^+ + 4Cl' \rightarrow (RuCl_5.OH)'' + 4H_2O$$
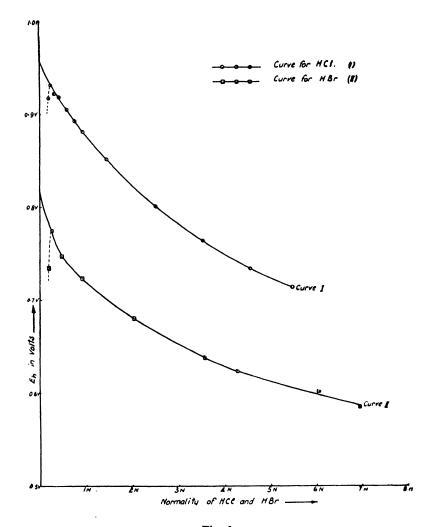
Fig. 1.

It is considered that the potential measured in dilute acid at the point where the maximum is reached is of the reaction

$$RuX.(OH)_2^+ + X' + 2H^+ + e' \rightarrow (RuX_2)^+ + 2H_2O.$$
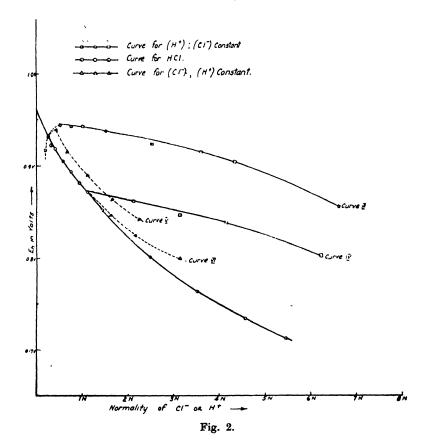
The potential extrapolated from this point to zero acid concentration, for the chloride system was 0.96 ± 0.002 volt, and for the bromo system 0.82 ± 0.002 volt.

<div align="center">EXPERIMENTAL.</div>

Oxidant and Reductant Solutions.

Potassium pentachlorohydroxy ruthenate IV was prepared by the method of Charonnat (*loc. cit.*) from the pure metal. The purplish brown crystals were recrystallised from normal hydrochloric acid, and dried in vacuum over sulphuric acid. The oxidant solution was made in oxygen-free normal hydrochloric acid, and was M/100. Solutions in 0·1 N acid darkened slightly on keeping, but in 0·20 N acid ruthenium dioxide gradually precipitated.

(*b*) *Potassium aquopentachloro ruthenate III* was prepared by taking a portion of the oxidant solution above, and allowing it to stand in an atmosphere of carbon dioxide in contact with silver

<div align="center">Fig. 2.</div>

wool. At the end of twenty-four hours, the colour had changed to yellow, and the precipitate of the silver halide had settled out. No trace of ruthenium metal was formed during the reduction. The reduced solution was kept over silver wool in the inert atmosphere.

(*c*) *Potassium pentabromohydroxy ruthenate IV.* This substance was prepared by the same method as the chloro compound, either by treatment of the potassium ruthenate with hydrobromic acid, or by fusion of ruthenium metal with potassium hydroxide and potassium bromate, followed by extraction with water and treatment with hydrobromic acid. The dark purplish brown crystals were recrystallised from dilute hydrobromic acid. The M/100 solution was made in normal hydrobromic acid.

(*d*) *Potassium aquopentabromo ruthenate III.* The reduction of the purple oxidant solution could not be performed with alcohol in the presence of hydrobromic acid, whilst in the absence of acid or in very dilute acid, hydrolysis caused the deposition of some ruthenium dioxide.

Reduction with silver wool gave the required pale yellow solution of the compound, but the reduction tended to form some bivalent ruthenium compound owing to the low potential of the reaction $Ag + Br' \rightarrow AgBr$ e'. However it was found that the colour change from yellow to the pale green of the ruthenium II compound was quite sharp, and thus by the addition of some of the oxidant solution it was possible to remove the bivalent state. The solution was stored in an atmosphere of carbon dioxide.

Apparatus. The redox assembly, with a saturated potassium chloride salt bridge, was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1944). The potential of the saturated calomel electrode was taken as $0 \cdot 2443$ volt at 25° C. The potentials on gold and platinum electrodes were measured on a Leeds and Northrup valve potentiometer, and are considered accurate to $\pm 2mv$.

Procedure. The oxidant solution (5 ml.) was mixed with acid, and distilled water in that order to prevent hydrolysis and made up to 35 ml. Where potassium chloride and ammonium sulphate were added, the dry salts were used, and dissolved at room temperature. The hydrobromic acid was freshly distilled, free from bromine, and was stored over carbon dioxide. The prepared solution was freed from traces of air by passage of carbon dioxide and the reductant solution (5 ml.) added. The final mixture was thus M/800 with respect to both oxidant and reductant. It was allowed to stand in an inert atmosphere for two weeks. When equilibrium had been established among the various ions, the mixture was placed in the redox vessel, previously filled with carbon dioxide, and allowed to come to equilibrium with the electrodes. During this time—usually 24 hours—the potential decreased slightly. Finally the salt bridge was inserted, and the equilibrium potential measured whilst the solution was stirred with a current of carbon dioxide. The results of the various measurements are shown in the foregoing tables and curves.

SUMMARY.

The potential of the quadrivalent/trivalent ruthenium couple has been studied in hydrochloric and hydrobromic acid solutions. From the shapes of the curves it is concluded that the system is cationic. The potential is depressed markedly by halide ions and to a lesser extent by hydrogen ions. The results are consistent with the existence of hydrated cations of the type $(RuX(OH)_2)^+$ and $(RuX.OH)^{++}$ for the oxidant and $(RuX_2)^+$ and $(RuX)^{++}$ for the reductant. The potentials for the chloro and bromo systems respectively, extrapolated from the point where hydrolysis becomes serious to zero acid concentrations are $0 \cdot 96 \pm 0 \cdot 002$ volt and $0 \cdot 82 \pm 0 \cdot 002$ volt.

REFERENCES.

Buividate, 1935. *Zeit. anorg. Chem.*, **222**, 279.
Charonnat, 1931. *Ann. Chim.*, **16**, 5.
Dwyer, McKenzie and Nyholm, 1944. *Ibid.*, **78**, 260.
———————————————— 1946. THIS JOURNAL, **79**, 183.
——.———————————— 1947. *Ibid.*, **81**, 216.
Dwyer, Humpoletz and Nyholm, 1947a. *Ibid.*, **80**, 242.
———————————————— 1947b. *Ibid.*, **80**, 212.
Grube and Fromm, 1940. *Zeit. fur Electrochem.*, **46**, 661.
——.——————— 1941. *Ibid.*, **47**, 208.
Grube and Nann, 1939. *Ibid.*, **45**, 871.
Howe, 1927. *J. Am. Chem. Soc.*, **48**, 2381.
Kolthoff and Tomsicek, 1935. *J. Phys. Chem.*, **39**, 945.
Morgan and Burstall, 1936. *J. Chem. Soc.*, 41.
Werner and Smirnoff, 1920. *Helv. Chim. Acta*, **3**, 737.

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THE CHEMISTRY OF RUTHENIUM.

PART V. THE POTENTIAL OF THE BIVALENT/TRIVALENT RUTHENIUM COUPLE IN HYDROCHLORIC ACID.

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When a solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid is treated with strong reducing agents such as zinc or lead, the deep brown colour changes successively to yellow, green, blue, and finally deposits the metal itself. The yellow solution contains trivalent ruthenium (Howe, 1927 ; Charonnat, 1931), but for a time a controversy existed over the green and blue substances, which were thought to contain respectively bivalent and monovalent ruthenium. According to Latimer (1940) the question has been definitely settled by the work of Crowell and Yost (1928), who showed that the blue solution contained the element in the bivalent state, whilst the green colour was due to a mixture of the trivalent and bivalent states. Recently, however, Grube and Nann (1939), as a result of the study of the electrolytic reduction of ruthenium trichloride in hydrochloric acid, claimed that the reduction proceeded to the bivalent state in concentrated acid, but in dilute acid the univalent state resulted. The reduction steps were identified by potentiometric titration with hydrogen peroxide. Univalent ruthenium was found to undergo disproportionation—$2Ru^+ \rightarrow Ru^{++} + Ru$; and the potential of the reaction $Ru^+ - e' \rightarrow Ru^{++}$ was found to be in the range $0 \cdot 03$ to $0 \cdot 05$ volt. The published titration curves, however, do not show well-marked inflexions ; the potentials from which the curves were obtained were almost instantaneous and not equilibrium values, and an irreversible oxidant was used. Additional evidence in substantiation of univalent ruthenium is therefore desirable.

The present investigation deals with the determination of the potential of the bivalent/trivalent ruthenium couple in hydrochloric acid with a view to checking the existence of the univalent state.

The mixed oxidant/reductant solution was prepared by the reduction of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid with pure lead foil in an oxygen-free atmosphere of carbon dioxide. The resulting deep blue solution contained 15–20% of bivalent ruthenium, whilst the remainder was trivalent. Although the lack of equimolarity in this solution involved a large correction to obtain the standard potential, the large excess of the trivalent state automatically eliminated the possibility of any of the alleged monovalent state being present. The reduced solution to which varying amounts of acid were added was allowed to come to equilibrium with a smooth gold electrode in an atmosphere of carbon dioxide. As soon as the potential reading was taken the concentration of bivalent ruthenium was determined by addition of a known volume of the solution to oxygen-free ferric alum solution. In this way an equivalent amount of ferrous salt was formed.

$$Ru^{++} + Fe^{+++} \rightarrow Ru^{+++} + Fe^{++}$$

From the present work it is known that the potential of the Ru^{II}/Ru^{III} system is of the order of $0 \cdot 1$ volt, whilst from the previous paper (This Series,

Part III) the potential of the Ru^{III}/Ru^{IV} system is approximately 0·9 volt, hence the ferric salt can only oxidise to the trivalent state. The partly reduced iron solution was then oxidised potentiometrically with potassium permanganate, the first step being due to oxidation of the ferrous ion. The total ruthenium in the solution was estimated by oxidation to the quadrivalent state with a slight excess of chlorine, followed by potentiometric titration with stannous chloride. The potential of the stannous/stannic system (0·13 volt; Latimer, 1940) is such that the reduction $2Ru^{4+}+Sn^{++}\rightarrow2Ru^{3+}+Sn^{4+}$ proceeds to completion without the formation of any bivalent ruthenium compound, or the separation of ruthenium metal. The difference in the total ruthenium concentration and the bivalent ruthenium concentration then gives the concentration of trivalent ruthenium.

The observed potentials were corrected to the standard equimolar potential by the usual equation. Since the activities of the oxidant and reductant were unknown, the observed concentrations were substituted.

The reduction of ruthenium tribromide in hydrobromic acid could be effected with either silver or lead, but the reduced solution was coloured green. Even when the reduction was carried out with zinc to the point where most of the metal was deposited, the colour remained green. It was concluded that the green colour was not due to admixture of the bivalent and trivalent states, but that the ionic species of bivalent ruthenium is not the simple hydrated Ru^{++} but hydrated $(RuBr^+)$ and $(RuCl)^+$. The determination of the potential of the green solution was not successful as a brown deposit formed on the electrode, whilst a satisfactory method could not be found for the estimation of the bivalent ruthenium. The potential of the trivalent/quadrivalent ruthenium couple in hydrobromic acid (approx. 0·7 volt) is almost the same as the ferrous ferric system. The reaction $Ru^{++}+Fe(CN)_6'''\rightarrow Ru^{3+}+Fe(CN)_6''''$, although theoretically feasible, proved to be unsuitable.

The potential of the chloride system was found to be almost independent of the acid concentration from 1·5 N to 6·8 N hydrochloric acid. Measurements in the lower acid concentrations could not be obtained owing to the separation of ruthenium on the electrode

$$3Ru^{++}\rightarrow Ru+2Ru^{+++}$$

From the independence of the potential on the ionic strength, it can be concluded that increasing ionic strength has the same effect on the activities of both the oxidant and the reductant, and hence that they probably carry the same charge. Since the lowest valencies of the metal are involved, the system is almost certainly cationic, and the equivalence of charge must be due to covalent bonding of part of the halogen. In Part III of this series evidence was put forward for the existence of ruthenium trichloride in dilute solution as either the hydrated ion $(RuCl)^{++}$ or $(RuCl_2)^+$, and from the behaviour of ruthenium tribromide towards reducing agents it is suggested that the reductant ion is $(RuCl)^+$. It is considered, therefore, that the redox reaction of the couple is

$$(RuCl_2)^++e'\rightarrow(RuCl)^++Cl'.$$

The potential of the trivalent/bivalent couple in 1·53 N acid, 0·084 volt is not very much higher than the potential of the alleged bivalent/monovalent couple measured by Grube and Nann (*loc. cit.*)—0·03 to 0·05 volt in 0·1 N acid. In solution containing small concentrations of hydrochloric acid, ruthenium trichloride is known to hydrolyse extensively (Grube and Fromm, 1940). As a result the potential of the Ru^3/Ru^2 system can be expected to be quite low in low concentrations of hydrochloric acid. It is also significant that the disproportionation, which was supposed to be due to univalent ruthenium, occurs with bivalent ruthenium in weakly acid solution. This could well arise by dissociation of the $(RuCl)^+$ ion to Ru^{++}, which undergoes disproportionation.

It is concluded from the present study that the univalent ruthenium ion has no existence in solution.

EXPERIMENTAL.

Oxidant and Reductant Solutions.

An M/50 solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid (2 N) was saturated with oxygen-free carbon dioxide and thin strips of lead foil added. After about thirty minutes the deep brown solution had become yellow and the reaction had almost stopped by the deposition of ruthenium on the lead. The solution was decanted on to fresh lead, and sealed in carbon dioxide until after 20–30 minutes a deep royal blue solution had formed. This was filtered from lead chloride and ruthenium metal through a sintered glass filter into a storage vessel, fitted with a burette, so that known volumes could be withdrawn without exposure to oxygen. Since the acid concentration had changed during the reduction by reaction with the lead, the acidity was determined by titration with sodium hydroxide and methyl orange indicator. The total ruthenium in the solution was estimated by dilution of a known volume with dilute hydrochloric acid and oxidation with a slight excess of chlorine water. The excess was then boiled out, and the solution potentiometrically titrated with standard stannous chloride. The excess of chlorine was such that any loss as ruthenium tetroxide could be regarded as negligible. The solution was found to be M/800 with respect to ruthenium.

Apparatus.

The redox apparatus was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1946). The saturated calomel electrode, taken as 0·2443 volt at 25° C., was connected to the cell through a saturated potassium chloride salt bridge. During the potential determinations the apparatus was sealed with apeizon wax and kept under a slight pressure of carbon dioxide.

Procedure.

An oxygen-free solution (30 ml.) of hydrochloric acid of the required concentration was saturated with carbon dioxide in the redox vessel, the reduced ruthenium solution (10 ml.) added quickly, and the apparatus sealed. After approximately 24 hours equilibrium had been attained, and the potential was measured with a Leeds and Northrup valve potentiometer. The system was unpoised and the ordinary potentiometer was unreliable. A portion of the solution (30 ml.) was immediately withdrawn through a stream of carbon dioxide and added to oxygen-free standard ferric alum solution. Potentiometric titration with potassium permanganate then gave the concentration of bivalent ruthenium at the equilibrium point.

The potential values at the various acid concentrations are shown in Table I.

TABLE I.

The Potential of the Ru^{II}/Ru^{III} System in Hydrochloric Acid.
Total Ru Concentration, $1 \cdot 25 \times 10^{-3}$ M.

Acid Concentration Normality.	E, Observed. (Volt.)	$[Ru^{++}] \times 10^{-3}$	$[Ru^{+++}] \times 10^{-3}$	E, Observed Corrected. (Volt.)	E_h. (Volt.)
1·53	—0·128	0·279	0·97	—0·160	0·084
2·6	—0·130	0·301	0·95	—0·160	0·084
2·6	—0·132	0·305	0·945	—0·161	0·083
3·64	—0·121	0·27	0·98	—0·154	0·090
5·22	—0·131	0·27	0·98	—0·164	0·080
6·8	—0·127	0·28	0·97	—0·157	0·087

SUMMARY.

The potential of the bivalent/trivalent ruthenium couple in hydrochloric acid was found to be $0 \cdot 084$ volt $\pm 0 \cdot 005$ volt in the hydrochloric acid range of concentrations from $1 \cdot 53$ N to $6 \cdot 8$ N. It is considered that the system is cationic with the ionic species $(RuCl_2)^+$ and $(RuCl)^+$ for the oxidant and reductant respectively. From the potential values and the behaviour of the system in low acid concentrations, it is concluded that Grube and Nann's alleged univalent ruthenium is really bivalent ruthenium.

REFERENCES.

Charonnat, 1931. *Ann. Chim.*, **16**, 5.

Crowell and Yost, 1928. *J. Am. Chem. Soc.*, **50**, 374.

Dwyer, McKenzie and Nyholm, 1946. THIS JOURNAL, **78**, 260.

Grube and Fromm, 1940. *Zeit. fur Electrochem.*, **46**, 661.

Grube and Nann, 1939. *Ibid.*, **45**, 871.

Howe, 1927. *J. Am. Chem. Soc.*, **48**, 2381.

Latimer, 1940. Oxidation Potentials. Prentice Hall, New York.

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KEPLER'S PROBLEM.

HARLEY WOOD, M.Sc.

Abstract.—Kepler's problem is reviewed from analytical and numerical standpoints, the region of usefulness of various solutions defined and formulae suggested for the nearly parabolic case. A bibliography is given.

The two body problem was solved (kinematically) by Kepler with the enunciation of his three laws of planetary motion which were later to be contained within the implications of the more general theory of gravitation. The Keplerian rules (regarded as derived from the gravitational equations) are still used in most derivations of the equations which connect the position variables of planetary motion with the time variable. The problem of finding the coordinates of a planet in the plane of its orbit in unperturbed motion is Kepler's problem.

If we express the equation of the solution path of planetary motion in a form using the parameters e (eccentricity) and q (perihelion distance) which apply equally to the three conics without involving infinite or imaginary values (as for example the major and minor axes would) and take x_0, y_0 as the rectangular coordinates in the plane of motion with the x_0 axis directed towards perihelion we obtain

$$x_0{}^2 + y_0{}^2 = \{q(1+e) - ex_0\}^2 \tag{1}$$

The equation for constancy of areal velocity is

$$x_0 y'_0 - x_0' y_0 = c$$

that is

$$2x_0 y_0' - (x_0 y_0)' = c$$

where the dashes indicate differentiation with regard to time.

Now if we write

$$\lambda = \frac{x_0}{q}, \quad \mu = \frac{y_0}{q} \text{ and } \varepsilon = \frac{1-e}{1+e} \tag{2}$$

and take the initial point at perihelion this becomes

$$\int_0^{\mu_1} 2q^2 \lambda \, d\mu - q^2 \lambda_1 \mu_1 = ct \tag{3}$$

and equation (1) gives

$$\lambda = \frac{1}{1-e}\{-e \pm (1-\varepsilon\mu^2)^{\frac{1}{2}}\} \tag{4}$$

In substituting (4) into (3) in the elliptic case the branch of λ corresponding to the upper sign must be used from perihelion ($\mu = 0, \lambda = 1$) to $\mu = \varepsilon^{-\frac{1}{2}}, \lambda = -e/(1-e)$ and that corresponding to the lower sign from this point to $\mu = 0, \lambda = -\varepsilon^{-1}$. In the hyperbolic case the lower sign corresponds to the non-solution branch of the hyperbola. The case $e = 1$ is obvious.

On integrating (3) in this way, putting $c = kq^{\frac{1}{2}}(1+e)^{\frac{1}{2}}$ from the dynamical theory where k is the Gaussian constant, we obtain

$$k(1+e)^{3/2}q^{-3/2}t = \varepsilon^{-3/2}\{\pm \sin^{-1}\varepsilon^{1/2}\mu - e\varepsilon^{1/2}\mu\} + C \tag{5}$$

where the subscript on μ may now be dropped without ambiguity. In the elliptic case we can without loss of generality take the positive sign and $C=0$ if we put $\sin^{-1}\varepsilon^{1/2}\mu > \pi/2$ in the interval in which μ is decreasing. The hyperbolic case requires only the upper sign.

From (4) we obtain

$$\lambda = 1 - \frac{\mu^2}{1+e}\frac{1 \mp (1-\varepsilon\mu^2)^{1/2}}{\varepsilon\mu^2}, \tag{6}$$

with the same remarks about signs. This will be found a convenient form for calculation.

Equation (5) will be taken as the general expression of Keplerian motion. If we put $\varepsilon^{1/2}\mu = \sin E$

$$M = ka^{-3/2}t = E - e\sin E, \tag{7}$$

where a is the semi-major axis, M the mean anomaly and E the eccentric anomaly.

When ε is negative put $\varepsilon = -\alpha = (e-1)/(e+1)$, $\sinh F = \alpha^{1/2}\mu$ and we obtain (since $\sin^{-1}i\alpha^{1/2}\mu = i\sinh^{-1}\alpha^{1/2}\mu$)

$$M = ka^{-3/2}t = e\sinh F - F. \tag{8}$$

Equation (5) may be written

$$D = 12k(1+e)^{1/2}q^{-3/2}t = 12\mu + \mu^3(1+\varepsilon)6\left(\frac{\sin^{-1}\varepsilon^{1/2}\mu - \varepsilon^{1/2}\mu}{\varepsilon^{3/2}\mu^3}\right), \tag{9}$$

which will be found a convenient expression for dealing with the nearly parabolic case (e near 1).

For the parabolic case ($e=1$)

$$12\sqrt{2}kq^{-3/2}t = 12\mu + \mu^3 \tag{10}$$

and if we place

$$\tan\frac{v}{2} = \tau = \tfrac{1}{2}\mu$$

we obtain

$$6k(2q)^{-3/2}t = 3\tau + \tau^3$$

which is the usual expression for parabolic motion, where v is the true anomaly.

Equation (7) is the one which now bears Kepler's name. It is an early example of a transcendental equation occurring in applied mathematics and very few men even as eminent as Kepler can have such an enduring memorial as this equation. The necessity for its frequent solution and the difficulties, numerical and analytical, which it presents have kept alive interest in the equation during the whole of the 300 years since its discovery. The analytical points involved if we wish to express the implicit function E of equation (7) explicitly as a series in M and e are of interest and consideration of them has been important in the development of the theory of analytic functions (see references in Wintner, 1941). The interval of convergence as a power series in e must depend on the singularities of the function $E = E(e, M)$ in the complex plane for e.

The function

$$e = \frac{E-M}{\sin E} \tag{11}$$

is a meromorphic function with simple poles at the points $\sin E = 0$ except when $E = M$.

The inverse function $E = E(e, M)$ must be multiple valued and the branch for which $e=0$ implies $E = M$, that is the branch in which we are interested,

is regular at $e=0$. The singularities of the inverse function are given by zeros of the derivative, that is by

$$\frac{1-e \ \cos \ E}{\sin \ E}=0$$

The singularities at $E=\infty$ correspond to connected paths to infinity (see Hurwitz, 1906) in the E plane for which e, given by (11), approaches a finite point. This only occurs for $e=0$ and therefore does not affect the branch in which we are interested, which is regular at this point. Hence the singularities are determined by (11) and the equation

$$M-E+\tan \ E=0 \qquad\qquad (12)$$

where M is real (in the elliptical case).

Every point on the real axis of e for which $|e| > 1$ is a branch point. Let us put $E=a+ib$ into equation (12) and equate real and imaginary parts giving

$$b=\frac{(1+\tan^2 \ a) \ \tanh \ b}{1+\tan^2 \ a \ \tanh^2 \ b}, \qquad\qquad (13)$$

$$-M+a=\frac{(1-\tanh^2 \ b) \ \tan \ a}{1+\tan^2 \ a \ \tanh^2 \ b},$$

from which

$$\tan^2 \ a=\frac{\tanh \ b-b}{(b \ \tanh \ b-1) \ \tanh \ b} \qquad\qquad (14)$$

and

$$(a-M)^2=(\tanh \ b-b)(b-\coth \ b) \qquad\qquad (15)$$

Equation (15) shows that b must lie between $-\beta$ and $+\beta$ where β is given by

$$\beta=\coth \ \beta$$

If, using equations (11) and (12), we write

$$\xi+i\eta=e=\sec \ E,$$

equate real and imaginary parts and use equation (13) we obtain

$$\left.\begin{array}{l} \xi=b \ \cos \ a \ \operatorname{cosech} \ b, \\ \eta=b \ \sin \ a \ \operatorname{sech} \ b. \end{array}\right\} \qquad\qquad (16)$$

If we now use b as a parameter equations (14) and (16) give the curve of singularities.

For the case of the hyperbola M is replaced by iN (with N real); equation (12) becomes

$$-iN+E-\tan \ E=0$$

and any real value of e for which $|e| \leqslant 1$ gives a solution (that is a singularity).

If as before we let $E=a+ib$, $e=\xi+i\eta$ the equations corresponding to (14), (15) and (16) are

$$\left.\begin{array}{l} \tanh^2 \ b=\dfrac{\tan \ a-a}{(1+\tan \ a) \ \tan \ a}, \\ (b-N)^2=(\tan \ a-a)(\cot \ a+a) \end{array}\right\} \qquad\qquad (17)$$

and

$$\left.\begin{array}{l} \xi=(b-N) \ \cos \ a \ \operatorname{cosech} \ b, \\ \eta=(b-N) \ \sin \ a \ \operatorname{sech} \ b. \end{array}\right\} \qquad\qquad (18)$$

The curves (symmetrical about both axes) of singularities for the ellipse and the hyperbola are shown in Figure 1, where the dashed line refers to the

ellipse and the dotted line to the hyperbola. The curve for the ellipse was first discussed by T. Levi-Civita (1904a) and C. V. L. Charlier (1904) (the work of the latter not having been available to me) and the hyperbola by H. G. Block (1904). Other discussions are given by H. Andoyer (1923) and A. Wintner (1941).

For elliptic motion the nearest singular point to the origin is on the imaginary axis at a point given by

$$\beta = \coth \beta$$

$$\eta = \beta \ \text{sech} \ \beta = 0 \cdot 6627 \ . \ . \ .$$

The power series expression for E in elliptic motion is convergent uniformly with M only for $0 \leqslant e < 0 \cdot 6627 \ . \ . \ .$ In both cases the curve is incident with real axis at an angle of $\pi/3$ and in the hyperbolic case the curve is assymptotic to the line $\xi = \pi/2$.
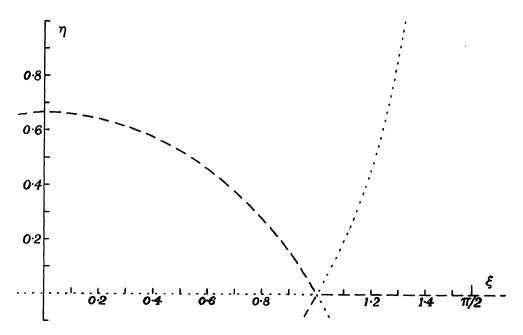
Fig. 1.—Curves of singularities in the complex e plane (first quadrant) for solutions of elliptical and hyperbolic motion.

In the case of hyperbolic motion the curve of singularities shows that no development in e or $1/e$ converges for all values of M and even the development in powers of $e - e_0$ ($e_0 > 1$) is of no practical use for the circle of convergence (uniformly with M) is limited by the curve and cannot include the region near $e = 1$, the cusp of the curve.

Turning to equation (10) for parabolic motion μ is seen to be a three valued function of $D = 12\sqrt{2}kq^{-3/2}t$. For D real there are two complex roots and one real, the real root increasing monotonically with D. The zeros of the first derivative of $12\mu + \mu^3 + D$ occur at $\mu = \pm 2i$; the Riemann surface of $\mu = \mu(D)$ has branch points at $D = \pm 16i$ and there are no further finite singularities. These singularities limit the radius of convergence and the general usefulness of any development of (the real branch of) μ according to powers of $D - D_0$.

Turning to the nearly parabolic case write equation (9) in the form $F(\varepsilon, \mu, D)=0$. Expanding $\sin^{-1} \varepsilon^{1/2}\mu$ as a series we obtain

$$0 = -D + 12\mu + \mu^3(1+\varepsilon)6\left(\frac{1}{2.3} + \frac{1.3}{2.4}\frac{\varepsilon\mu^2}{5} + \ldots\right),\tag{19}$$

where the right-hand member is an expression of part of the branch of $F(\varepsilon, \mu, D)$ for which $\mu=0$ implies $D=0$ (for $|\varepsilon\mu^2| < 1$). For this branch of $F(\varepsilon, \mu, D)$ the origin is a regular point but it is a pole for every other branch.

Also we have

$$\frac{\partial F}{\partial \mu} = 12 + (1+\varepsilon)\frac{6}{\varepsilon}\{(1-\varepsilon\mu^2)^{-1/2}-1\}\tag{20}$$

$$= 12 + \mu^2(1+\varepsilon)6\left(\tfrac{1}{2} + \frac{1.3}{2.4}\varepsilon\mu^2 + \ldots\right).$$

This shows that for D, ε and μ real we have

(i) When $0 \leqslant e < 1$, the elliptical case, i.e. $1 \geqslant \varepsilon > 0$ F is monotonic increasing with μ for $\varepsilon\mu^2 < 1$,

(ii) When $e \geqslant 1$, the parabolic (see equation 10) and hyperbolic cases, $0 \geqslant \varepsilon > -1$ F is monotonic increasing with μ and there is a unique real solution of (9) for any real value of D. We also see that for small values of ε there are always solutions of $\partial F/\partial\mu = 0$ near the points $\mu^2 = -4$ on the imaginary axis of μ. The existence of these singularities limits the radius of convergence and usefulness of the development of μ as a power series in D with coefficients in ε (fixed). The attempt to express the coefficient of μ^3 in (9) as a development in series in order to evaluate the coefficient and transform the equation for solution into an ordinary cubic meets with the same difficulty.

However, let us consider $\mu = \mu(D, \varepsilon)$ as a function of ε (D real constant) and wish to develop the solution as a Taylor's series proceeding in powers of ε with coefficients functions of $\nu = \mu(D, 0)$. It will be necessary to see how the matter is affected by singularities of $\mu = \mu(D, \varepsilon)$ for ε in the complex domain in the vicinity of the solution $\varepsilon = 0$, $\mu = \nu$ on the real axis.

Let us write equation (20) in the form

$$\frac{1}{12}\frac{\partial F}{\partial \mu} = 1 + \tfrac{1}{2}\left\{\frac{1-(1-\varepsilon\mu^2)^{1/2}}{(1-\varepsilon\mu^2)^{1/2}}\right\} + \frac{\mu^2}{4} + \frac{\mu^2}{4}\left\{\frac{2[1-(1-\varepsilon\mu^2)^{1/2}]}{\varepsilon\mu^2(1-\varepsilon\mu^2)^{1/2}} - 1\right\}$$

$$= 1 + f_1(\varepsilon\mu^2) + \frac{\mu^2}{4} + \frac{\mu^2}{4}f_2(\varepsilon\mu^2)$$

Now for the points $\varepsilon = 0$, $\mu = \nu$, $1 + \mu^2/4 \neq 0$ and $f_1(\varepsilon, \mu) = 0$, $f_2(\varepsilon, \mu) = 0$. Then if m is the lower bound of $|1 + \mu^2/4|$ on the circle $|\mu - \nu| = r$ about $\mu = \nu$ it is necessarily possible to choose r, so that $m > 0$. It is also possible to choose ρ such that $|\varepsilon| < \rho$ makes $f_1(\varepsilon, \mu) + f_2(\varepsilon, \mu) < m$. Hence by Rouché's theorem $\partial F/\partial\mu$ has within the domains $|\mu - \nu| < r$, $|\varepsilon| < \rho$ the same number of zeros as $1 + \mu^2/4$ and since ν is a point on the real axis with no zeros in its vicinity this can be made no zeros. The radius of convergence of the series for μ in ε thus shown to exist can be proved at least sufficient for practical needs.

Choose the circle round ν to be

$$\mu = \nu(1 + e^{i\varphi}/5)\tag{21}$$

(e here and for the rest of this paragraph is the exponential). Then the real part of $1 + \mu^2/4$

$$= 1 + \frac{\nu^2}{4} + \frac{\nu^2}{10}\cos\varphi + \frac{\nu^2}{100}\cos 2\varphi$$

$$> 1 + \frac{14}{100}\nu^2.$$

On this circle $f_1(\epsilon\mu^2) + \dfrac{\mu^2}{4} f_2(\epsilon\mu^2)$

$$= f_1(\epsilon\mu^2) + \frac{\nu^2}{4}\left(1 + \frac{2}{5}e^{i\varphi} + \frac{1}{25}e^{2i\varphi}\right)f_2(\epsilon\mu^2),$$

the modulus of which

$$\leqslant |f_1(\epsilon\mu^2)| + \frac{\nu^2}{4}\,\frac{36}{25}\,|f_2(\epsilon\mu^2)|.$$

Now consider $\epsilon\mu^2$ as the other variable (instead of ϵ). Since the coefficients of $\epsilon\mu^2$ in the series for f_1 and f_2 are positive numbers the maxima of the moduli of the functions for $|\epsilon\mu^2| = \rho$ occur on the positive real axis—that is for $\epsilon\mu^2 = \rho$. Take $\rho = 0\cdot35$, then

$$|f_1| < 0\cdot12, \quad |f_2| < 0\cdot38$$
$$|f_1 + f_2| < |1 + \mu^2/4|$$

whence

So that $\partial F/\partial\mu$ has the same number of zeros in the circle (21) with $\epsilon\mu^2$ in the domain $|\epsilon\mu^2| \leqslant 0\cdot35$ as has $1 + \mu^2/4$—that is none—and there are no singularities for the values of ϵ and μ satisfying the given conditions. We shall see later that the nearly parabolic solution is not required for $|\epsilon^{1/2}\mu| > 0\cdot58$—that is $|\epsilon\mu^2| > 0\cdot34$.

The solution of (19) may now be obtained as a Taylor's series of the form

$$\mu = C_0 + C_1\epsilon + C_2\epsilon^2 + \ldots \tag{22}$$

either by calculating the necessary differential coefficients or by equating coefficients taking $D = 12\nu + \nu^3$, ν being the solution for $\epsilon = 0$. If this is done we find

$$C_0 = \nu$$
$$C_1 = -\frac{\nu^3}{1 + \nu^2/4}\left(\frac{1}{2^2.3} + \frac{3}{2^4.5}\nu^2\right)$$
$$C_2 = -\frac{\nu^5}{(1 + \nu^2/4)^3}\left(\frac{1}{2^2.3.5} + \frac{127}{2^5.3^2.5.7}\nu^2 + \frac{1}{2^4.5.7}\nu^4 - \frac{1}{2^9.5^2.7}\nu^6\right)$$

The disadvantage of this method of solution is that even in the range of appropriateness of the nearly parabolic solution ν may become large and the tabulation for the coefficients correspondingly extended.

The form of the equations determining the coefficients in (22) suggests another solution. The equation determining C_1 is of form

$$C_1(1 + \nu^2/4) = -\nu^3 \quad \text{(polynomial of degree 2 in } \nu\text{)}.$$

The polynomial has no term of the first power in ν, so that if we divide throughout by $1 + \nu^2/4$ we can obtain a remainder of the form $\gamma_1\nu^3$ where γ_1 is a numerical constant, so that if we add a term $\gamma_1\nu^3\epsilon$ to the $12\nu + \nu^3$ side of the original equation the coefficient of ϵ would become a polynomial of degree 2 and γ_1 a constant to be determined in the process of equating coefficients. Similarly it is possible to obtain a form of coefficient avoiding fractions for the higher powers of ϵ by equating coefficients in a solution of the form

$$D = 12\sigma + \sigma^3 c^2$$
$$= 12\mu + \mu^3(1 + \epsilon)6\left(\frac{1}{2.3} + \frac{1.3}{2.4}\,\frac{\epsilon\mu^2}{5} + \ldots\right),$$
$$c^2 = 1 + \gamma_1\epsilon + \gamma_2\epsilon^2 + \ldots,$$
$$\mu = \sigma(1 + G_1\epsilon + G_2\epsilon^2 + \ldots),$$

with

$$G_1 = g_{12}\sigma^2,$$
$$G_2 = g_{22}\sigma^2 + g_{24}\sigma^4,$$
$$\cdots$$

$$\left.\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array}\right\} \tag{23}$$

where G_n is a polynomial of degree $2n$ in σ an auxiliary quantity determined by the first equation. Here the first coefficients are

$$G_1 = -\frac{3}{2^2.5}\sigma^2,$$

$$G_2 = -\frac{1}{2.5^2.7}\sigma^2 + \frac{1}{2^3.5^2.7}\sigma^4,$$

$$G_3 = -\frac{13}{3^2.5^3.7}\sigma^2 + \frac{71}{2^3.3^2.5^3.7}\sigma^4 + \frac{1}{2^4.3^2.5^2.7}\sigma^6,$$

$$G_4 = -\frac{107}{2^2.3^2.5.7^2.11}\sigma^2 + \frac{6679}{2^4.3^2.5^3.7^2.11}\sigma^4 + \frac{221}{2^6.5^3.7^2.11}\sigma^6 + \frac{43}{2^8.5^3.7^2.11}\sigma^8,$$

$$G_5 = -\frac{2^9.103}{3.5^5.7^2.11.13}\sigma^2 + \frac{214601}{2^4.3^2.5^5.7.11.13}\sigma^4 + \frac{178849}{2^6.3^2.5^5.7^2.11.13}\sigma^6$$
$$+ \frac{123791}{2^8.3^2.5^5.7^2.11.13}\sigma^8 + \frac{1213}{2^8.3^2.5^5.7.11.13}\sigma^{10},$$

$$c^2 = 1 - \frac{4}{5}\varepsilon - \frac{6}{5^2.7}\varepsilon^2 - \frac{52}{3.5^3.7}\varepsilon^3 - \frac{107}{3.5.7^2.11}\varepsilon^4 - \frac{2^{11}.103}{5^5.7^2.11.13}\varepsilon^5 \cdot \cdot \cdot ,$$

where the exponent is placed on c so that the first equation can be conveniently written in the same form as that for the parabola and solved by the use of the same table. The extreme value of ε for which the nearly parabolic solution is necessary is $0 \cdot 07$, for which the first neglected term of c^2 is $0 \cdot 8 \times 10^{-9}$.

In the process leading to the previous solution it would have been possible to carry on the division by $(1 + \nu^2/4)$ a step further to give a remainder of the form $\beta_1 \nu$ and destroyed the fractional form of the C_1 term in the solution in Taylor's series by adding a term $\beta_1 \nu \varepsilon$ to the left-hand member of the equation determining the coefficients. This suggests a solution of the form

$$12\tau + \tau^3 b = 12\mu + \mu^3(1 + \varepsilon)6\left(\frac{1}{2.3} + \frac{1.3}{2.4}\frac{\varepsilon\mu^2}{5} + \cdot \cdot \cdot\right),$$

with
$$b = 1 + \beta_1\varepsilon + \beta_2\varepsilon^2 + \cdot \cdot \cdot ,$$
$$\mu = \tau(1 + H_1\varepsilon + H_2\varepsilon^2 + \cdot \cdot \cdot),$$

where H_n is a polynomial of degree $2n$ in τ. The first terms of this solution are given by

$$H_1 = \frac{4}{3.5} - \frac{3}{2^2.5}\tau^2,$$

$$H_2 = \frac{242}{3^2.5^2.7} - \frac{43}{2.5^2.7}\tau^2 + \frac{1}{2^3.5^2.7}\tau^4,$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$b = 1 + \frac{4}{3.5}\varepsilon + \frac{242}{3^2.5^2.7}\varepsilon^2 + \cdot \cdot \cdot$$

It is a pleasure to acknowledge the helpful conversations I had with Mr. W. B. Smith-White, who kindly read a draft of this section before it was offered as a contribution to him in his capacity of editor.

NUMERICAL CONSIDERATIONS.

Kepler's equation may for purposes of calculation be written in a number of ways according to the tastes of the computer or the tables he has available; among these are

$$[M] + \{e\}(\sin E) = E$$

$$-\left[\frac{M}{e}\right] + \left\{\frac{1}{e}\right\}(E) = \sin E$$

$$[M] + \{e\}(Y) = \sin^{-1} Y$$

$$[M] - \{1 - e\}(Y) = \sin^{-1} Y - Y$$

where $\sin E = Y$. The quantity in the square bracket is put into the product register of the calculating machine, that in the curly bracket in the setting register and the quantity in the plain bracket built up in the multiplier register till the right-hand member of the equation appearing in the product register has the value corresponding to that in the plain bracket. The first two forms, due to Comrie and Strömgren respectively (see Möller, 1933), require a table of sines with argument in decimals of a degree or in radians. The recently published Chambers Six-Figure Mathematical Tables (Comrie, 1949) are most suitable. Reasonably near to perihelion the third and fourth forms are useful. The tables of Möller (1940) and Strömgren (1945) are particularly suitable for the last form, which is valuable in the range of values, to be discussed shortly, when computation with an extra figure is necessary. The last three forms have the advantage that the quantity to appear in the multiplier register, being the argument of the mathematical table, can be more conveniently built up to its full number of tabulated figures. It should be added that the second method can be used even if e is small, since although its reciprocal is large and the significant figures of E/e and M/e are moved relative to those $\sin E$ the same thing occurs with the equation in its original form and indeed (if only E were required) for a five-figure solution of $M = E - e \sin E$ with $e < 0 \cdot 1$ the value of $\sin E$ would be needed to only four decimals.

If the tables for $\sin E$ extend only to $\pi/2$ the equation may be used past this point in the form

$$(\pi - M) - e \sin (\pi - E) = \pi - E$$

or

$$\frac{\pi - M}{e} - \frac{\pi - E}{e} = \sin (\pi - E)$$

It is well known that the accuracy of solution of Kepler's equation falls off when e tends towards 1. Suppose equation (7) has been solved by using a table of sines. Let the solution obtained be E_1, $\sin_t E_1$ the value of its sine simultaneously obtained from the table and E the accurate solution.

Then

$$M = E_1 - e \sin_t E_1,$$

$$\sin_t E_1 = \sin E_1 + \triangle,$$

$$E_1 = E + \delta E,$$

and

$$\sin_t E_1 = \sin E + \delta \sin E$$

where the last three equations are definitions of $\triangle$, the error of the table and of δE and $\delta \sin E$, the errors in the solutions for E and $\sin E$ respectively. From these equations with (7)

$$\delta E = \frac{e \triangle}{1 - e \cos E} \quad \text{and} \quad \delta \sin E = \frac{\triangle}{1 - e \cos E}$$

If we are working with a table to n figures the maximum error (now called $\triangle$) of the table will be $0 \cdot 5 \times 10^{-n}$ and its average value would be half of this.

The rectangular coordinates in the plane of the orbit are

$$x_0 = a \ (\cos E - e)$$
$$y_0 = a(1 - e^2)^{1/2} \ \sin E$$

and the maximum errors in these arising from errors in solving Kepler's equation and (another $\triangle$) in extracting cos E from the tables are

$$\delta x_0 = a \triangle (e \ \sin E + 1 - e \ \cos E)/(1 - e \ \cos E)$$
$$\delta y_0 = a(1 - e^2)^{1/2} \triangle /(1 - e \ \cos E)$$

The effect that these errors has on the position of a body on the celestial sphere depends on their relation in direction and magnitude to the geocentric distance vector, but as this relation differs for every body and for the same one at different times it is best for the purpose of establishing a measure of the influence of the errors on the position of an object to compare their magnitude with that of the heliocentric distance, r. Now

$$r = a(1 - e \ \cos E)$$

so that using the relations above

$$\frac{\{(\delta x_0)^2 + (\delta y_0)^2\}^{1/2}}{r} = \frac{(2 + 2e \ \sin E)^{1/2}}{(1 - e \ \cos E)^{3/2}} \triangle \qquad (24)$$

The value of the coefficient of $\triangle$ in (24) which may be tolerated is arbitrary, but 3 seems a reasonable figure and one which will not introduce errors from this cause more serious than must be admitted in almost any extended calculation. If the values of M and e are plotted as abscissa and ordinate on a plane, the curve given by (7) and

$$\frac{(2 + 2e \ \sin E)^{1/2}}{(1 - e \ \cos E)^{3/2}} = 3$$

defines the boundary of the region in which Kepler's equation will give a satisfactory result. Beyond this region is an area in which it is profitable if we want a result accurate to n figures to work with a table to $n + 1$ decimals. The boundary of this region is given by

$$\frac{(2 + 2e \ \sin E)^{1/2}}{(1 - e \ \cos E)^{3/2}} = 30$$

and beyond this methods adapted for nearly parabolic solutions should be used.

Also consider the equation

$$x_0 = a(\cos E - e)$$

and suppose the possible error in the tabulation of cos E to be $\triangle_1$, then

$$\delta x_0/r = \triangle_1/(1 - e \ \cos E) \qquad (25)$$

along the extra figure boundary $(1 - e \ \cos E)^{-1}$ has values from $1 \cdot 8$ to $2 \cdot 5$ and along the nearly parabolic boundary from $7 \cdot 8$ to $8 \cdot 5$, which shows that it is necessary to work with the extra figure, when it is appropriate, even after the determination of E (or sin E). For small geocentric distances, say less than $0 \cdot 3$ astronomical unit, it would be necessary to use the extra figure apart from the considerations arising above.

If we work through the case of the hyperbolic orbit, equation (8), in the same way as has been done for the ellipse we find the boundary beyond which extra figure computation is necessary is given by

$$\frac{(2e \ \cosh F + 2e \ \sinh F)^{1/2}}{(e \ \cosh F - 1)^{3/2}} = 3$$

and that beyond which nearly parabolic solution must be used by

$$\frac{(2e \text{ cosh } F + 2e \text{ sinh } F)^{1/2}}{(e \text{ cosh } F - 1)^{3/2}} = 30$$

Both equations are taken with equation (8) if M is to be plotted against e.

Figure 2 shows these curves which define the regions in which the various types of computation are appropriate. In Figure 3 the area in which nearly parabolic solution is desirable is represented on the plane of e and sin E ($= \varepsilon^{1/2}\mu$) M and sin E are always available when calculating in the ordinary way or with
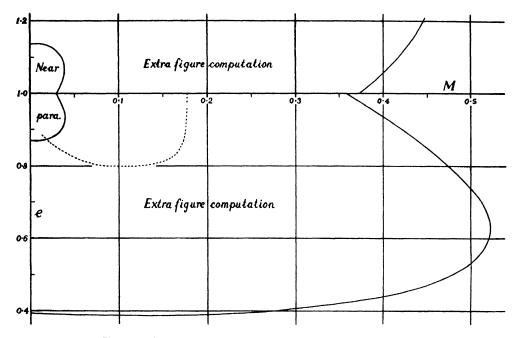
Fig. 2.—Method of solution according to values of e and M.

the extra figure and a quantity approximating to $\varepsilon^{1/2}\mu$ is available at a stage in the nearly parabolic solution which I hope to publish soon so that these diagrams facilitate a decision as to which type of computation is to be used, or in some cases when a change of process is necessary. In doubtful cases either of the possible alternatives should be satisfactory. It may be pointed out that the nearly parabolic solution is not necessary except when sin $E < 0.53$ or sinh $F < 0.58$ and by the previous discussion the development in series of the solution for the co-ordinate μ is then permissible.

Many transformations of Kepler's equation have been used to provide solutions, ones of importance being by Tietjen (see Bauschinger, 1934), Howe (see Plummer, 1919) and Oppolzer and Marth (see Marth, 1890b). Oppolzer and Marth, independently, wrote the equation in the form

$$\tan (E - M) = \frac{e \text{ sin } M}{\lambda - e \text{ cos } M},$$

where

$$\lambda = \frac{E - M}{\sin (E - M)}.$$

Tables for this solution were given by the two authors mentioned and more recently Subbotin (1929) has used it tabulating log λ to seven decimal places

with argument tan $(E-M)$.   It is of interest to examine the range of applicability of this transformation of Kepler's equation as was done for the equation itself in the previous paragraphs.

We obtain

$$\delta E = \frac{\tan (E-M)}{\sec^2 (E-M)\{\cos (E-M)+(E-M) \sin (E-M)-e \cos M\}}\Delta$$

$$= \frac{\frac{1}{2} \sin 2 (E-M)}{\cos (E-M)+(E-M) \sin (E-M)-e \cos M}\Delta$$

Where Δ is the error of the tabulated value of λ.   The ratio of the error arising from δE in the position of the body on the plane of its orbit to the radius vector
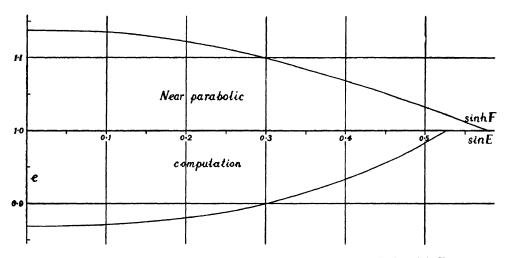
Fig. 3.—Method of solution according to values of e and sin E (or sinh F).

is

$$\frac{\{(\delta x_0)^2+(\delta y_0)^2\}^{1/2}}{r} = \left\{\frac{1+e \cos E}{1-e \cos E}\right\}^{1/2}\delta E \qquad (26)$$

$$= \left(\frac{1+e \cos E}{1-e \cos E}\right)^{1/2} \frac{\frac{1}{2} \sin 2 (E-M)}{\cos (E-M)+(E-M) \sin (E-M)-e \cos M}\Delta$$

If we are prepared to allow the coefficient of Δ in this equation to attain the value 3 and as before map the boundary of the area for which the transformation is applicable, we are applying a rather less severe test since the error in the equation includes the effect arising only from the error in calculating E and neglects errors in the tables subsequently used for computing x_0 and y_0.   Nevertheless, the boundary which is shown by the dotted curve on Figure 2 indicates that while the method of solution does represent an improvement on that using a table of sines to the same number of figures, it does not improve on the accuracy obtained by using the sine table to an extra figure nor encroach appreciably on the area in which a nearly parabolic solution is needed.

It is thus not possible to dispense with extra figure calculation unless we are willing to extend unduly the tabulation for nearly parabolic solutions. Equations (25) and (26) show that however accurately E may be determined the solution in terms of eccentric anomaly leads to difficulties when e is nearly 1 and E is small.

BIBLIOGRAPHY.

The following bibliography is supplementary to the references given by Radau (1900), Bauschinger (1901 and 1934), Herglotz (1906) and Wintner (1941). Material listed by these authors has not been repeated unless referred to in my article. The titles of the references do not always show satisfactorily the aspect of Kepler's Problem with which they deal, so they are omitted and the contents indicated by a code, which has the further advantage of economy.

G, indicates a general account such as might be given by a text book, a review article or an article chiefly didactic in purpose,

T, that the main interest is theoretical,

S, an article whose main purpose is to describe or discuss a method of obtaining a solution of Kepler's Problem, and

I, a solution depending on numerical integration or the application of finite differences.

e, indicates that the article refers to elliptic motion,

n, to nearly parabolic motion, and

p, to parabolic motion.

s, indicates a solution in power series,

f, a solution in trigonometric series,

g, that the solution is graphical or mechanical and

c, that a numerical solution is given (c is only used if two methods are described otherwise solutions may be assumed to involve numerical methods),

t, indicates that tables are given to aid the purpose of the article and

z, that I have not seen the article myself and depend on a review or abstract for its description.

This bibliography is meant to be fairly comprehensive for categories S and T. Developments whose main application lies in the study of perturbed motion have usually been omitted except for some borderline cases under the heading I. The historical aspect has been neglected entirely but those who are interested will find valuable guidance in Radau (1900), Herglotz (1906) and Wintner (1941); and the bibliography of Houzeau and Lancaster (1887, 1889) gives many references, nearly all of which were inaccessible to me. The collected works of Kepler have been edited by Frisch (1858-71) and a recent account of " de motibus stellae Martis " is given by Pannekoek (1948).

Adams, C. E., 1921. *Hector Obs. Bull.*, **37**, G.

Adams, J. C., 1883. *Mon. Not. R. ast. Soc.*, **43**, 365. Se.

Aldis, W. S., 1902. *Mon. Not. R. ast. Soc.*, **62**, 633. Sct.

Andoyer, H., 1923. Cours de mécanique Céleste, Gauthier-Villars, Paris, Gt.

Bauschinger, J., 1901. Tafeln zur Theoretischen Astronomie, Engelmann, Leipzig. Gt.

———————— 1934. Second edition of Bauschinger, 1901, edited by G. Stracke. Gt.

Baženow, G., 1929. *Astr. Nachr.*, **234**, 425 Seg.

Block, H. G., 1904. *Ark. Mat. Astr. Fys.*, **1**, 467. Also *Medd. Lunds astr. Obs.*, 23. T.

Bobone, J., 1930. *Revista Astronomica Buenos Aires*, **2**, 398. Sez.

Brenke, W. C., 1936. *Pop. Astr.*, **44**, 76, Te.

Brouwer, D., 1937. *Astr. J.*, **46**, 149. I

Brown, E. W., 1931. *Mon. Not. R. astr. Soc.*, **92**, 104. Se.

Brown, E. W., and Shook, C. A., 1933. Planetary Theory, Cambridge Uni. Press. G.

Burckhardt, J. C., 1815. Connaiss. Temps for 1818, 319. Spt.

Charlier, C. V., 1904. *Medd. Lunds astr. Obs.*, 22. Tz.

Chrétien, H., 1908. *C.R. Ass. Franç. Av. Sci.*, **36**, 83. Seg.

Comrie, L. J., 1949. Chamber's Six-Figure Mathematical Tables, Chambers, London.

Cowell, P. H., and Crommelin, A. C. D., 1910. Obsns. Greenw., 1909, Appendix I.

Crawford, R. T., 1930. Determination of Orbits of Comets and Asteroids, McGraw-Hill, New York. Gt.

Creedy, C., 1857. *Quart. J. pure appl. Math.*, **1**, 259. Sf.

Crommelin, A. C. D., 1896. *J. Brit. astr. Ass.*, **6**, 105. Sp.
———————————— 1916. *J. Brit. astr. Ass.*, **26**, 150. G.
———————————— 1922. *J. Brit. astr. Ass.*, **32**, 305. Sp.
Davidson, M., 1934. *Mon. Not. R. astr. Soc.*, **95**, 66. Sn.
Dazew, A., 1934. *Astr. Nachr.*, **253**, 191. Seg.
Dolainski, F., 1913. *Astr. Nachr.*, **194**, 43. Seg.
Draper, G. H., 1936. *Astr. J.*, **45**, 140. Set.
Englefield, H. C., 1793. On the Determination of the Orbits of Comets, Peter Elmsly, London. Spt.
Fleckenstein, J. O., 1941. *Comment. math. helvet.*, **13**, 83. T.
Frisch, C., 1858-71. Joannis Kepleri Astronomi Opera Omnia, 8 vols., Frankofurti et Erlangæ. z.
Fry, T. C., 1916. *Astr. J.*, **29**, 141. Seg.
Gasparis, A. de, 1857. *Mon. Not. R. astr. Soc.*, **17**, 155. Se.
——————————— 1862. *Mon. Not. R. astr. Soc.*, **23**, 20. Se.
——————————— 1877. *Mon. Not. R. astr. Soc.*, **37**, 263. Se.
Gaythorpe, S. B., 1919. *J. Brit. astr. Ass.*, **30**, 94. Se.
Germay, R. H. J., 1932. *Bull. Acad. Belg. C. Sc.*, Ser. V, t 17, 1180, also Université de Liège, Institut d'Astronomie et de Géodésie, 80. Te.
Gonggrijp, B., 1901. *Astr. Nachr.*, **155**, 369. Seg.
Hagihara, Y., 1935. *Proceedings of the Imperial Academy of Japan*, **11**, 93, also *Annals of Tokyo astr. Obs.*, 45, Tz.
——————————— 1936. *Astr. J.*, **45**, 129. T.
Hall, A., 1905. *Pop. Astr.*, **13**, 287. Sef.
Halley, E., 1749. Tabulæ Astronomicæ, London. Sptz.
——————————— 1752. Astronomical Tables. London. Sptz.
Hansen, P. A., 1852. *Mon. Not. R. astr. Soc.*, **13**, 52. Sef.
Hartmann, J., 1918. *Astr. Nachr.*, **205**, 309. Se.
Herget, P., 1936. *Publ. Cincinn. Obs.*, 21. Snt.
Herglotz, G., 1906. *Encyklopädie der Mathematischen Wissenschaften* VI, 2 Teil, 379. G.
Herrick, S., 1945. *Astr. J.*, **51**, 123. Sn.
Hillebrand, C., 1908. *Denkschr. Akad. Wiss. Wien.*, **84**, 15. I.
——————————— 1909. *Denkschr. Akad. Wiss. Wien.*, **85**, 61. I.
Houzeau, J. C., and Lancaster, A., 1887 and 1889. Bibliographie Générale de L'Astronomie, Imprimeur de L'Academie Royale de Belgique, Bruxelles
Howe, H. A., 1919. *Pop. Astr.*, **27**, 569 Se.
——————————— 1922. *Pop. Astr.*, **30**, 161. Se.
Humbert, P., 1933. *Publ. Obs. Astr. Univ. Belgrade, Mémoires*, **2**, 11. nz
Hurwitz, A., 1906. *C.R. Acad. Sci., Paris*, **143**, 877. Te.
Innes, R. T. A., 1924. *Astr. J.*, **36**, 39. Se.
——————————— 1926. *Astr. Nachr.*, **228**, 265. I.
——————————— 1926. Circ. Un. Obs., Johannesb., 71, with appendix. I and Set.
——————————— 1933. *Observatory*, **56**, 61. Se and p.
Iwanow, A., 1901. *Nachrichten der Russischen Astromischen Gesellschaft*, **8**, 95. Tez.
Jackson, J., 1924. *Mon. Not. R. astr. Soc.*, **84**, 602. I.
Langebartel, R. G., 1948. *Astr. J.*, **53**, 101. Se.
Laska, V., 1914. *Astr. Nachr.*, **199**, 295. Seg.
Le Grand Roy, E., 1903. *Arch. Sci. phys. nat.*, **16**, 328. Seg.
Levi-Civita, T., 1904a. *Accad. Lincei. Sed. solenni.*, **13**, 260. T.
——————————— 1904b. *Astr. Nachr.*, **165**, 313. T.
Levin, A. E., 1922. *Mon. Not. R. astr. Soc.*, **82**, 177. Seg.
Mache, H., 1910. *Astr. Nachr.*, **186**, 357. Se.
Marth, A., 1890a. *Mon. Not. R. astr. Soc.*, **50**, 502. Seft.
——————————— 1890b. *Mon. Not. R. astr. Soc.*, **50**, 530. Set.
Merlin, E., 1930. Comptes rendus du Congrès national des Sciences, Bruxelles, 1930, p. 495. Sez.
Merton, G., 1926. *J. Brit. astr. Ass.*, **36**, 151. It.
Matkiewicz, L., 1922. Jahresbericht 1921, der Sternwarte Pulkowa, appendix. Snz.
Matussowitsch, N. N., 1929. *Mitt. russ. Hauptstern. Pulkowo*, **11**, 242. Se.
Möller, J. P., 1933. *Mon. Not. R. astr. Soc.*, **93**, 777. Snt.
——————————— 1940. Festschrift für Elis Strömgren, Munksgaard, Copenhagen, p. 163. Set.
Morrison, J., 1883. *Mon. Not. R. astr. Soc.*, **43**, 345 and 494. Se.
Moulton, F. R., 1895. *Pop. Astr.*, **3**, 136. Seg.
——————————— 1907. *Astr. J.*, **25**, 145. Se.
——————————— 1914. An Introduction to Celestial Mechanics, Second Edition, MacMillan, New York. G.
——————————— 1930. *Revista Astronomica, Buenos Aires*, **2**, 409. Segz.
Noumeroff, B., 1923. *Trud. glav. ross. astrofiz. obs.*, 2. I.
——————————— 1924. *Russ. Astr. J.*, **1**, Part 2, 87. I.
——————————— 1924. *J. Observateurs*, **7**, 125. It.

Pannekoek, A., 1948. *Pop. Astr.*, **56**, 63.
Picart, L., 1906. *Bull. Astr. Paris*, **23**, 353. Se.
Plummer, H. C., 1896. *Mon. Not. R. astr. Soc.*, **56**, 317. Seg.
————— 1906. *Mon. Not. R. astr. Soc.*, **67**, 67. Seg.
————— 1918. An Introductory Treatise on Dynamical Astronomy, Cambridge University Press. G.
————— 1919. *Mon. Not. R. astr. Soc.*, **80**, 207. Se.
Poincaré, H., 1905. Leçons de Mécanique Céleste, Gauthier-Villars, Paris. G.
Porro, F., 1900. *G. Mat.*, **38**, 10. ez.
Radau, R., 1900. *Bull. astr., Paris*, **17**, 37.
Rakowiecki, T., 1929. *Wiad. mat.*, **31**, 1. Sez.
Rambaut, A. A., 1890. *Mon. Not. R. astr. Soc.*, **50**, 301. Seg.
————— 1906. *Mon. Not. R. astr. Soc.*, **66**, 519. Seg.
————— 1913. *Astr. J.*, **27**, 182. Seg.
Rand, W. C., 1942. *J. Brit. astr. Ass.*, **52**, 149. Seg.
Rasmusen, H. Q., 1936. *Astr. Nachr.*, **260**, 325. It.
Rust, F., 1908. *Pop. Astr.*, **16**, 36. Se.
Sconzo, P., 1933. *Mem. Soc. astr. ital.*, **7**, 59. STz.
————— 1933. *Atti. Accad. " Nuovi Lincei ",* **86**, 55. Se.
————— 1934. *Atti. Accad. " Nuovi Lincei ",* **87**, 490. Sef.
————— 1934. *Mem. Soc. astr. ital.*, **7**, 421. Sfz.
Searle, G. M., 1889. *Astr. J.*, **8**, 153. Snt.
————— 1892. *Astr. J.*, **11**, 89. Sn.
See, T. J. J., 1895. *Mon. Not. R. astr. Soc.*, **56**, 54. Seg.
Smiley, C. H., 1934. *Mon. Not. R. astr. Soc.*, **95**, 63. Sn.
Stracke, G., 1934. See Bauschinger, J., 1934.
Strömgren, B., 1945. Mémoires de L'Institut Géodésique de Danemark, Ser. 3, Vol. 15. Optical Sine Tables.
Stumpff, K., 1947. *Astr. Nachr.*, **275**, 108. Sent.
Subbotine, M. T., 1928. *Russ. astr. J.*, **5**, 207. Set.
Subbotin, M. T., 1929. *Publ. Obs. astr. Tashkent*, 2. Gt.
————— 1933. *Poulkovo Obs. Circ.*, **9**, 15. It.
Tisserand, F., 1889. Traité de Mécanique Céleste, Gauthier-Villars et Fils, Paris. G.
Trayler, M. C., 1901. *Pop. Astr.*, **9**, 311. G.
Trousset, J., 1911. *Bull. astr. Paris*, **28**, 389. Te.
Udick, Stella, 1912. *Astr. J.*, **27**, 97. Set.
Ueta, Y., 1927. *Mon. Not. R. astr. Soc.*, **87**, 207. Seg.
Viaro, B., 1920. *Atti Isti. veneto*, **79²**, 965. Sez.
Wallace, W., 1836. *Mem. R. astr. Soc.*, **9**, 185. Se.
Wedemeyer, A., 1918. *Astr. Nachr.*, **206**, 147. Se.
Weiler, A., 1899. *Astr. Nachr.*, **150**, 247. Se.
Wilczynski, E. J., 1912. *Astr. J.*, **27**, 155. Seg.
————— 1913. *Astr. J.*, **27**, 185. Seg.
Wilkens, A., 1918. *Astr. Nachr.*, **206**, 21. Se.
Willis, J. E., 1929. *Astr. J.*, **39**, 117. Se.
Wintner, A., 1941. The Analytical Foundations of Celestial Mechanics, Princeton University Press, Princeton. T.
Wirtz, C., 1918. Tafeln und Formeln aus Astronomie und Geodäsie, Springer, Berlin. Gt.
Wirtz, C., and Hügeler, P., 1918. *Siriuskalender für* 1919, 61. Sptz.
Witt, G., 1906. *Astr. Nachr.*, **172**, 129. Se.
————— 1931. *Astr. Nachr.*, **241**, 9. Sn.
Wood, H. E., 1926. *J. Brit. astr. Ass.*, **36**, 149. I.
Wood, H. W., 1946. This JOURNAL, 79, 153, also Sydney Obs. Papers No. 1. Seg.
Zenger, C. V., 1882. *Mon. Not. R. astr. Soc.*, **42**, 446. Se.

A NEW METHOD OF MEASUREMENT OF THE SURFACE TENSION OF VISCOUS LIQUIDS.

By P. R. Johnson, B.Sc.

and R. C. L. Bosworth, D.Sc.

INTRODUCTION.

The measurement of the surface tension of viscous liquids, such as molasses, by usual methods, is often hindered by factors arising from the high viscosity of the liquid. Thus L'eaute (1935) in measuring the surface tension of tars and bitumen by capillary rise, notes that equilibrium condition for bitumen is reached in 360 hours. In the Sugden bubble pressure method, the time required to blow the bubble with no viscosity interference is of the order of ten minutes, an unpracticably long time. With the Du Nouy tensiometer, the break point for molasses is poorly defined.

The method now presented is a development of the Eötvös reflection method for sessile drops and is independent of viscosity. It may be applied to the measurement of the surface tension of liquids in general, with particular value for viscous liquids such as molasses and other concentrated sugar syrups.

Previous methods of measuring surface tension from the shape of sessile drops have relied on actual measurement of radii of curvature and other drop dimensions, usually made on the profile of the drop. Thus Worthington (1881) projected the form of *hanging* drops of water on a screen and measured radii of curvature and the volume of the drop. His work was amplified by Ferguson (1912), who photographed the drop. Moser (1927) calculated surface tensions from observations made vertically on sessile drops, and proposed refinements of the original method used by Eötvös (1886). Moser's observations were made with a telescope, to measure the vertical distance between two points of reflection on the curved surface of the drop and also the angles at which the light was reflected. Kemball (1946) employed side view illumination and a comparator for measuring sessile drops of mercury, and calculated the surface tension from the height and equatorial diameter of the drop. Taylor and Alexander (1944) also used side view illumination. They photographed sessile drops formed on the end of a brass tube and, from the photograph, measured the height of the drop above its equatorial plane, the equatorial diameter and thence calculated the surface tension.

EXPERIMENTAL.

In the method now presented, a drop of liquid on a plane surface (not wetted by the liquid) is illumined from above by two point sources of light, and photographed by a camera placed between the lights. A millimetre scale is also included in the photograph, which shows the images of the lights reflected by the drop. The distance between these images is measured by reference to the photographed millimetre scale. The equatorial diameter of the drop is also measured from the photograph. The distance from the light to the drop, and the distance between the lights are also measured. Figure 1, which is not

drawn to scale, illustrates the method of deriving the radius of curvature of the drop from these measurements.

From a consideration of the similar triangles L_1L_2F and I_1I_2F, we get

$$\frac{a}{x} = \frac{y}{\text{focal length}}$$

$$= \frac{y}{\frac{1}{2}b}$$

$$\text{Then } b = \frac{2xy}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where b = the radius of curvature at the vertex of the drop.

x = the distance of the drop from the light.

y = the distance between the images on the drop.

a = the distance between the lights.

x and a are large in comparison with b and y. In the actual apparatus x was 68 cm., a was 47 cm., while b and y were usually of the order of 0·3 cm.

The value of b thus found, together with r, the equatorial radius of the drop (measured from the photograph) is then used to calculate the surface tension by means of a formula,

$$\text{Surface tension} = \gamma = \frac{r^3}{b-r} \times \frac{dg}{6} \text{ dynes cm.}^{-1}.$$

where d = density difference between liquid and surrounding gas, in gm. cm.$^{-3}$.

g = gravitational acceleration in cm. sec.$^{-2}$.

DEDUCTION OF THE FORMULA.

The formula above was obtained from a study of the tables of Bashforth and Adams (1883). These tables give the values of b/x at a series of values of a dimensionless quantity, defined as

$$\beta = \frac{gdb^2}{\gamma}$$

where b is the radius of curvature at the vertex of the drop and γ is the surface tension.

x is the horizontal distance from the surface of the drop to its axis. The maximum value of x we have designated as r and thus obtained values of b/r as an empirical function of β. Empirically it has been found that there is an almost linear relationship between β and $\frac{b^2}{r^2}\left(\frac{b}{r}-1\right)$ and the ratio $\dfrac{\beta}{\dfrac{b^2}{r^2}\left(\dfrac{b}{r}-1\right)}$.

has an almost constant value of 6·0 over the range $0 < \beta < 4$. This ratio $\dfrac{\beta}{\dfrac{b^2}{r^2}\left(\dfrac{b}{r}-1\right)}$

cancels to $\dfrac{r^3}{b-r}\dfrac{dg}{\gamma}$ which we will designate as α. Values of β, $\dfrac{b^2}{r^2}\left(\dfrac{b}{r}-1\right)$ and

this quotient α are given in Table I.

PP

TABLE I.

Values of the Dimensionless Quantities Concerned with the Shape of Drops Calculated from the Tables of Bashforth and Adams.

$\beta = \dfrac{gdb^2}{\gamma}$	$\dfrac{b^2}{r^2}\left(\dfrac{b}{r}-1\right)$	$\alpha = \left(\dfrac{r_3}{b-r}\dfrac{dg}{\gamma}\right)$
0·1	0·01656	6·037
0·2	0·03316	6·031
0·3	0·049735	6·032
0·4	0·06626	6·036
0·5	0·08275	6·042
0·6	0·099245	6·045
0·7	0·115755	6·047
0·8	0·13226	6·049
0·9	0·14879	6·049
1·0	0·16533	6·049
1·2	0·19845	6·047
1·4	0·231675	6·043
1·6	0·26497	6·038
1·8	0·29836	6·033
2·0	0·331845	6·027
2·2	0·36543	6·020
2·4	0·29910	6·013
2·6	0·43290	6·006
2·8	0·46675	5·999
3·0	0·50073	5·991
4·0	0·67207	5·952
5·0	0·84569	5·912
6·0	1·0214	5·874
7·0	1·1991	5·837
8·0	1·3787	5·802
9·0	1·56015	5·768
10·0	1·7431	5·737
15·0	2·68035	5·596
20·0	3·6494	5·480

It will be seen that for the range $\beta = 0\cdot1$ to $\beta = 4\cdot0$ the proportionality factor is $6\cdot00 \pm 1$ per cent. maximum variation.

Thus

$$\frac{r^3}{b-r}\frac{dg}{\gamma} = 6\cdot0$$

or

$$\gamma = \frac{r^3}{b-r}\frac{dg}{6\cdot0} \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

where γ=the surface tension in dynes cm.$^{-1}$.
   r=the equatorial radius of the drop in cm.
   b=the radius of curvature at the vertex of the drop in cm.
   g=the gravitational acceleration in cm. sec.$^{-1}$.
   d=density difference between liquid and surrounding gas in gm. cm.$^{-3}$.

This equation used in conjunction with (1) provides an easy method of determining the surface tension from the measurement of the images reflected in sessile droplets.

Maximum Size of Drops.

   In using the equation

$$\gamma = \frac{r^3}{b-r}\frac{dg}{6\cdot0}$$

It is necessary for the drops to conform to the requirement that β be not greater than $4\cdot0$. This is evident from Table I, and therefore places an upper limit on the size of the drop. This maximum size can be deduced in the following manner :

The upper limit of the size of the drop depends on the surface tension and the density of the liquid under investigation.

Taking as the limiting condition

$$\beta = 4\cdot0$$

i.e.

$$g\frac{db^2}{\gamma} = 4\cdot0$$

this gives the limiting value of b as

$$b = \sqrt{\frac{4\gamma}{gd}}$$

Substituting this value of b in equation (2), we get

$$\frac{r^3}{2\sqrt{\dfrac{\gamma}{gd} - r}} \cdot \frac{gd}{\gamma} = 6\cdot0$$

whence

$$gdr^3 + 68r - 12\sqrt{\frac{\gamma^3}{gd}} = 0 \quad \dots\dots\dots\dots\dots\dots (3)$$

This is an expression for the limiting radius (r) of the droplet.

On substituting the approximate values for the density and surface tension of the liquid concerned, this equation may be solved numerically to give the maximum value of r.

Thus, for one of the more viscous liquids which it is proposed should be examined by this method, namely molasses, we have approximately

$$d = 1\cdot4 \text{ gm. cm.}^{-3}$$
$$\gamma = 65 \text{ dynes cm.}^{-1}.$$

Substituting these values in equation (3), we get

$$1372r^3 + 390r - 169\cdot6 = 0$$

or

$$r = 0\cdot320 \text{ cm.}$$

This means that the approximation implicit in equation (2) may be used with molasses for all drops up to a limiting diameter of $6\cdot4$ mm. This is quite a reasonably large drop.

For ethyl alcohol, a liquid with a low specific cohesion, we have

$$d = 0\cdot8 \text{ gm. cm.}^{-3}$$
$$\gamma = 22 \text{ dynes cm.}^{-1}.$$

Substituting these values in (3) and solving for r as above, we obtain

$$r = 0\cdot246 \text{ cm.}$$

Thus the maximum diameter of a drop of ethyl alcohol to be tested by this method is $0\cdot49$ cm.

Taking mercury as an example of a liquid with high surface tension, we have

$$d = 13\cdot6 \text{ gm. cm.}^{-3}$$
$$\gamma = 488 \text{ dynes cm.}^{-1}$$

from which the maximum value of r is $r = 0\cdot281$ cm., whence the maximum diameter is $0\cdot56$ cm.

In all cases examined it seems that the proposed method can be used over a reasonable range of drop diameter.

CAMERA.

L_1

L_2

PERP PERP PERP

S_1 O S_2

I_1 F I_2

R

LEGEND

L_1. L_2. ARE THE LIGHTS.

I_1 I_2 ARE THE IMAGES OF THE LIGHTS.

S_1 S_2. ARE POINTS ON SURFACE OF DROP ON LINES $L_1 S_1$ R & $L_2 S_2$ R

F. IS THE FOCAL CENTRE OF THE VERTEX OF THE DROP.

R. IS THE CENTRE OF CURVATURE OF THE DROP.

NOTE! AS $L_1 S_1$ & $L_2 S_2$ ARE VERY LARGE IN PROPORTION TO RADIUS OF CURVATURE. $R S_1$ & $R S_2$, THEN THE IMAGES WILL BE HALF WAY ALONG $R S_1$ & $R S_2$.
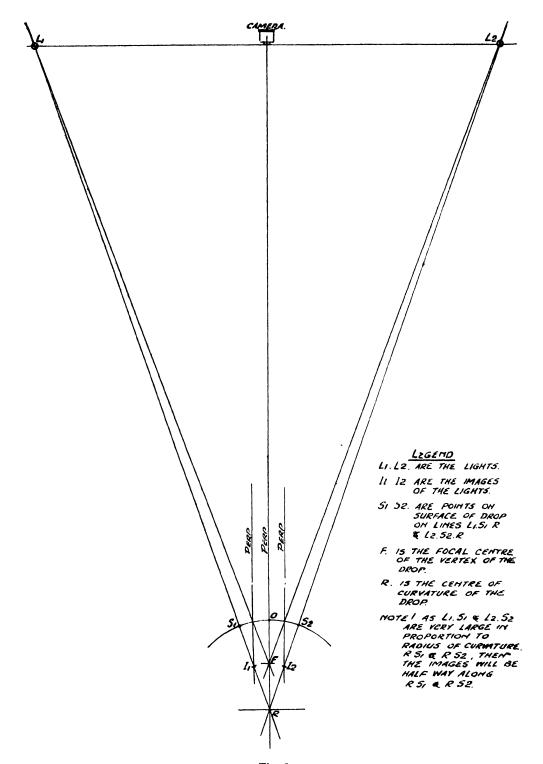
Fig. 1.

DISCUSSION.

The method proposed for the measurement of surface tension involves the measurement on a sessile drop, of the equatorial radius (r) and the radius of curvature at the vertex (b). It has been shown that these two quantities are related to the surface tension (γ), and the density of the liquid by the simple approximate formula

$$\gamma = \frac{r^3}{b-r} \frac{dg}{6}$$

This equation holds with an accuracy of 1 per cent. for all droplets below a certain limiting size. This limiting size depends on specific cohesion of the liquid concerned.

The method is particularly valuable for viscous liquids, since, being essentially a static method, it avoids errors arising from the slow attainment of equilibrium in such more familiar methods as the drop weight, ring, capillary rise and bubble pressure methods.

The experimental method is outlined in this paper and consists essentially of photographing a droplet of the liquid, illumined by two point sources of light. The results obtained from the examination of a number of standard liquids, by this method, will be presented in a later paper.

BIBLIOGRAPHY.

Bashforth, F., and Adams, J. C., 1883. An Attempt to Test the Theories of Capillary Action Cambridge University Press.

Eötvös, R., 1886. *Wied. Ann.*, **27**, 448.

Ferguson, A., 1912. *Phil. Mag.*, **23**, 417.

Kemball, C., 1946. *Trans. Farad. Soc.*, **42**, 526.

L'eaute, A., 1935. *Compt. Rend.*, **201**, 41.

Moser, H., 1927. *Ann. Physik.*, **82**, 963.

Pfund, A. H., and Greenfield, E. W., 1936. *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 81.

Taylor, H. J., and Alexander, J., 1944. *Proc. Indian Acad. Sci.*, **19A**, 149.

Worthington, A. M., 1881. *Proc. Roy. Soc. Lond.*, **A 32**, 362.

THE CHEMISTRY OF RUTHENIUM.

PART VI. THE EXISTENCE OF THE TRIS-O-PHENANTHROLINE RUTHENIUM II AND TRIS-O-PHENANTHROLINE RUTHENIUM III IONS IN ENANTIOMORPHOUS FORMS.

By F. P. DWYER, D.Sc.,
and (MISS) E. C. GYARFAS, M.Sc.

The resolution of tris 2 : 2′ dipyridylruthenium II bromide into optical forms of great stability was achieved by Burstall (1936), through the tartrate, thus demonstrating the octahedral distribution of the groups about hexacovalent bivalent ruthenium. Recently, the analogous tris o-phenanthroline compounds, $Ru(phenan)_3X_2$, were isolated (Dwyer, Humpoletz and Nyholm, 1946), but although the complexes were of great stability, and obviously of similar composition to the dipyridyl compounds, attempts at resolution through the tartrate, acid tartrate, bromcamphorsulphonate, and camphorsulphonate failed. In this paper the resolution of the tris o-phenanthroline complexes, through the antimonyl tartrate, is described.

When a solution of potassium antimonyl tartrate was added to a solution of tris o-phenanthroline ruthenium II chloride an orange crystalline precipitate resulted. This was found to be the almost pure d, tris-o-phenanthroline ruthenium II antimonyl tartrate, whilst the residual solution was strongly laevo rotatory. The conditions of precipitation were not critical, since the antimonyl tartrate of the d form appeared to be very insoluble, whilst the antimonyl tartrate of the l form was very soluble. Addition of a very large excess of potassium antimonyl tartrate failed to precipitate the laevo form. The crystalline d form was too insoluble in water to be crystallised easily, but was purified by solution in dilute alkali, followed by reprecipitation with acetic acid. The optically active acid radicle was eliminated from the purified material by solution in alkali and precipitation of either the perchlorate or iodide by the addition of sodium perchlorate or potassium iodide. These salts could be crystallised from water, but the perchlorate was the more suitable from the point of view of solubility. The perchlorate of the laevo form was obtained from the original laevo chloride solution by the addition of sodium perchlorate, and crystallised several times from warm water.

The optical forms were notably stable and could be crystallised repeatedly from hot water or alcohol, dissolved in six normal sulphuric acid or kept in aqueous solution at room temperature for over two months without change of rotation. The specific rotations of the forms were as follows : $[\alpha]_D^{20} = +1340°$ and $-1328°$; and $[\alpha]_{5461}^{20} = +2559°$ and $-2550°$. It is thus evident that the substance has a very large abnormal rotatory dispersion, and probably, when the complete rotatory dispersion curve is obtained, an anomalous rotatory dispersion. Burstall found $[\alpha]_{5791}^{25} = +860°$ and $-815°$ for the dipyridyl compound. It is probable that this substance too possesses an abnormal rotatory dispersion.

The optical forms were oxidisable with ceric nitrate to the blue ruthenium III complex, which was unstable except in high concentrations of acid (Dwyer, Humpoletz and Nyholm, 1946). The potential of the reaction $Ru(phenan)^{++}$ d or l form $-e' \rightarrow Ru(phenan)^{+++}$ in six normal sulphuric acid at 0° C. was found to be $1 \cdot 17$ volts $\pm 0 \cdot 003$ volt. The same value was obtained from the racemate by determining the potential with a mixture of the two optical forms. (See also Dwyer, 1949.) This is the first occasion that the redox potential of an enantiomorphous form has been compared with the racemate. It is unfortunate that the instability of the system precluded a more accurate value of the potentials.

When d or l tris-o-phenanthroline ruthenium II perchlorate in six normal sulphuric acid was oxidised with ceric nitrate the resulting blue solution containing the tris-o-phenanthroline ruthenium III ion was found to be optically active, but the rotation was different. The activity was lost rapidly at 20° C., but if the solution was immediately reduced with ferrous sulphate, the active ruthenium II compound was regenerated with its rotation unchanged. Since the ruthenium III complex could not be isolated the specific rotation has been calculated for the ion $Ru(phenan)_3^{+++}$. For comparison the rotation of the ion $Ru(phenan)_3^{++}$ are also calculated.*

Ion.	Na$_D$.	Hg$_{5461}$.
d $Ru(phenan)_3^{++}$	$+1834°$	$+3494°$
l $Ru(phenan)_3^{++}$	$-1818°$	$-3482°$
d $Ru(phenan)_3^{+++}$	$+584°$	$+2330°$
l $Ru(phenan)_3^{+++}$	$-568°$	$-2354°$

It is evident that the ion $Ru(phenan)_3^{+++}$ also has an abnormal rotatory dispersion. The resolution of hexacovalent ruthenium III complexes has already been carried out by Werner and Smirnoff (1920) and Charonnat(1931). The present observations are of particular interest, however, in that they provide a unique demonstration of the similarity of the oxidised and reduced forms of the o-phenanthroline complex, as well as of the essential simplicity of the oxidation/reduction reaction.

Preliminary experiments with the d form of the dipyridyl complex ion $Ru(dipy)_3^{++}$ show that this is also oxidisable with persistence of the optical activity, but the sign of the rotation is changed on oxidation. The results of the experiments on this compound, the resolution of the nickel and ferrous tris-o-phenanthroline complexes, and the complete rotatory dispersion curves for a number of such complexes will be published in subsequent communications.

EXPERIMENTAL.

(A 2 dm. tube was used for all determinations of the rotation.)

d-Tris-(o-Phenanthroline)-Ruthenium II d-Antimonyl Tartrate Dihydrate.

Tris-o-phenanthroline ruthenium II iodide (Dwyer, Humpoletz and Nyholm, 1946), $1 \cdot 3$ g., was dissolved in 100 mls. of hot water, and excess of silver chloride added. The mixture was shaken for five to ten minutes to transform the iodide to the chloride, and filtered with the addition

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* In making the transformation from the specific rotations of the salts to the specific rotations of the ions in the preliminary note to *Nature*, 163, 918 (1949) an error was made in the calculations.

of filter paper pulp. Potassium antimonyl tartrate (0·5 g.) in 30 mls. of water was added slowly to the cold chloride, with scratching. The voluminous orange-yellow precipitate was washed several times with water and dissolved with shaking in 75 mls. of cold N/20 sodium hydroxide. Dilute acetic acid was then added until acid, and a small volume of potassium antimonyl tartarte solution, when the substance reprecipitated as orange prismatic needles. It was insoluble in alcohol and sparingly soluble in water, but dissolved easily in the presence of a trace of alkali.

A 0·02% solution in M/100 NaOH gave $\alpha = +0·30°$, whence $[\alpha]_D^{20} = +750°$.

Found : N = 6·84% ; Sb = 19·45%.

Calculated for $[Ru(Cl_{12}H_8N_2)_3][SbO.C_4H_4O_6]2H_2O$: N = 6·82% ; Sb = 19·48%.

d-Tris-(o-Phenanthroline) Ruthenium II Perchlorate Monohydrate.

The d-antimonyl tartrate (0·6 g.) was dissolved in N/20 caustic soda (50 mls.) and the solution filtered. Sodium perchlorate solution (3 N approx.) was added slowly in excess, and the resulting orange-yellow precipitate filtered and washed with ice water containing a little perchloric acid. It was finally crystallised twice from warm water containing a trace of perchloric acid. Alternatively it could be crystallised from warm methanol by the addition of ether. The substance gave micro prismatic needles, which were easily soluble in warm water and alcohol. It was much more soluble than the perchlorate of the racemate.

A 0·205% solution in water gave $\alpha_D = +0·55°$ and $\alpha_{5461} = +1·05°$; whence $[\alpha]_D^{20} = +1340°$ and $[\alpha]_{5461}^{20} = +2560°$.

Found : Ru = 11·7% ; N = 9·87%.

Calculated for $[Ru(C_{12}H_8N_2)_3][(ClO_4)_2.H_2O]$: Ru = 11·8% ; N = 9·78%.

l-Tris-(o-Phenanthroline) Ruthenium II Perchlorate Monohydrate.

The original solution left after addition of potassium antimonyl tartrate contained approximately half of the substance taken, and was strongly laevo. It was treated with a further portion of antimonyl tartrate solution containing 0·4 g. and cooled in ice to remove traces of the d form. After filtration, the solution was treated with sodium perchlorate solution, and the resulting orange-yellow precipitate of the active perchlorate crystallised twice from warm water containing a trace of perchloric acid. The substance crystallised in orange-yellow micro prismatic needles.

A 0·0211% solution in water gave $\alpha_D = -0·56°$ and $\alpha_{5461} = -1·08°$; whence $[\alpha]_D^{20} = -1328°$ and $[\alpha]_{5461}^{20} = -2557°$.

Found : Ru = 11·9% ; N = 9·65%.

Calculated for $[Ru(C_{12}H_8N_2)_3][(ClO_4)_2.H_2O]$: Ru = 11·8% ; N = 9·78%.

The Redox Potentials of the d and l Forms and the Racemate.

Approximately M/800 solutions of the two optical forms as the perchlorates dissolved in sulphuric acid 6 N were placed in a redox assembly (Dwyer, 1949) and cooled to 0° C. Half of the theoretical amount of ceric nitrate solution necessary for the oxidation to the ruthenium III complex was added, and the maximum potential determined. For the potential of the racemate equal volumes of the d and l forms were mixed and treated as before with ceric nitrate.

$$d \text{ form} \quad : \quad E = 0·936 \text{ v.} ; \quad E_h = 1·169 \text{ v.}$$
$$l \text{ form} \quad : \quad E = 0·933 \text{ v.} ; \quad E_h = 1·166 \text{ v.}$$
$$\text{Racemate} : \quad E = 0·934 \text{ v.} ; \quad E_h = 1·167 \text{ v.}$$

Previous work on this system (Dwyer, Humpoletz and Nyholm, 1946 ; Dwyer, 1949) has shown that the potential is not reproducible to more than about 5 mv., so that it can be assumed that the potentials of the optical forms and the racemate are the same within the limits imposed by the instability of the system.

The Persistence of Optical Activity of the Complex Cation after Oxidation.

The d and l perchlorates in sulphuric acid 6 N were treated with drops of ceric nitrate (approx. 0·1 N in 1 N nitric acid) until the colour changed to blue. The amounts of oxidising agent needed were so small that the concentration change was neglected. The oxidised solution was immediately tested for optical activity, which was found to be still present, but the angle of rotation was smaller. A crystal of ferrous sulphate then added to each regenerated the complex ruthenium II cation, and the rotation rose to the original value.

A 0·0082% solution of the d perchlorate after oxidation gave $\alpha_D = +0·07°$ and $\alpha_{5461} = +0·28°$; whence the specific rotation of the d form of the ion $Ru(phenan)_3^{+++}$ $[\alpha]_D^{20} = +584°$ and $[\alpha]_{5461}^{20} = +2330°$.

A 0·0084% solution of the l perchlorate after oxidation gave $\alpha_D = -0·07°$ and $\alpha_{5461} = -0·29°$; whence the specific rotation of the l form of the ion $Ru(phenan)_3^{+++}$ $[\alpha]_D^{20} = -568°$ and $[\alpha]_{5461}^{20} = -2354°$.

SUMMARY.

The resolution of tris-o-phenanthroline ruthenium perchlorate has been carried out through the antimonyl tartrate. The enantiomorphous forms were notably stable, and showed a very large abnormal rotatory dispersion. They were oxidisable to the blue tris-o-phenanthroline ruthenium III cation, which was also optically active. Within the limits imposed by the instability of the system, the redox potentials of the enantiomorphous forms and the racemate were the same.

ACKNOWLEDGEMENTS.

REFERENCES.

Burstall, 1936. *J. Chem. Soc.*, 172.
Charonnat, 1931. *Ann. Chim.*, 16, 5.
Dwyer, Humpoletz and Nyholm, 1946. THIS JOURNAL, 80, 212.
Dwyer, 1949. *Ibid.*, 83, 134.
Werner and Smirnoff, 1920. *Helv. Chim. Acta.*, 3, 737.

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THE CHEMISTRY OF RUTHENIUM.

PART VII. THE OXIDATION OF D AND L TRIS 2 : 2′ DIPYRIDYL RUTHENIUM II IODIDE.

By F. P. DWYER, D.Sc.,

and (MISS) E. C. GYARFAS, M.Sc.

In previous papers (Dwyer and Gyarfas, 1949) it was shown that when d and l tris-o-phenanthroline ruthenium II perchlorates were oxidised with ceric nitrate, the resulting blue solutions of the tris-o-phenanthroline ruthenium III ion were still optically active, but the angles of rotation for the mercury line 5461 and the sodium D line were considerably smaller. It was inferred from these observations that the rotations of the complex ions in the oxidised and reduced forms were not necessarily different but that both ions possessed very large abnormal rotatory dispersions.

The oxidation of the d and l forms of the analogous tris-2 : 2′-dipyridyl ruthenium II ion has now been studied, and it is found that the rotation persists as before but that the sign is changed.

$$d\ Ru(dipy)_3^{++}\ \ (orange) \rightarrow l\ Ru(dipy)_3^{+++}\ (blue) + e'$$

$$and\ \ \ l\ Ru(dipy)_3^{++}\ \ \ \ \ \ \ \ \ \rightarrow d\ Ru(dipy)_3^{+++}\ \ \ \ \ \ \ + e'$$

After reduction the original ruthenium complex is regenerated, unaltered in the sign or magnitude of the rotation. This unique effect is due to anomalous rotatory dispersion, for the orange ruthenium II complex ion shows no absorption maximum in the visible, whilst that of the blue ruthenium II complex ion is at 5600 Å. The complete absorption and rotatory dispersion curves of this and the analogous iron, osmium and nickel compounds will be described in subsequent communications.

Burstall (1936) resolved tris-2 : 2′-dipyridyl ruthenium II bromide hexahydrate, $Ru(dipy)_3Br_2.6H_2O$ and found $[\alpha]_{5791}^{25} = +860°$ and $-815°$. The separation was achieved by the use of ammonium d and l tartrates, since the pure laevo form could not be obtained from the mother liquors from which the less soluble d-tris-dipyridyl ruthenium II d tartrate had been crystallised. Since ammonium l tartrate was unavailable it was necessary to devise another procedure for the isolation of the pure laevo form. This was carried out either by fractional crystallisation of the antimonyl tartrate, when the laevo form crystallised first and the dextro form was subsequently isolated as the d tartrate ; or more expeditiously as the lattice compound laevo

$$\{2Ru(dipy)_3(SbOTart)_2.Ru(dipy)_3I_2\}.18H_2O$$

This curious substance which could be recrystallised either from potassium iodide or potassium antimonyl tartrate solution, crystallised out first when potassium iodide was added to the mixed antimonyl tartrates. It can also be prepared directly by adding potassium antimonyl tartrate to the racemic iodide.

Experimental.

The Resolution of Tris-2 : 2-Dipyridyl Ruthenium II Iodide.

The racemic iodide $Ru(dipy)_3I_2.3H_2O$ was prepared as described previously (Dwyer, 1949). The iodide (2 g.) in hot water (150 mls.) was transformed to the antimonyl tartrate by shaking with silver antimonyl tartrate (0·9 g.) and filtering from silver iodide and the slight excess of silver antimonyl tartrate. The bright orange-red solution was evaporated to 60 mls. and cooled when 1 $Ru(dipy)_3(SbO.Tart)_2$ crystallised out. The red crystals were freed from adherent liquid between filter papers, dissolved in N/100 sodium hydroxide (100 mls.) (to destroy the antimonyl tartrate radicle) and precipitated as the iodide by fractional addition of potassium iodide solution. The laevo form was found in the least soluble fractions and purified by recrystallisation from hot water. The mother liquors from the initial antimonyl tartrate solution were precipitated with potassium iodide, and the resulting iodide transformed to the chloride by shaking with silver chloride. The solution of the chloride was then treated with ammonium d tartrate and the dextro form isolated as described by Burstall (*loc. cit.*).

The alternative method, which was found to be more efficient, consisted in taking the antimonyl tartrate solution (100 mls.) prepared from the racemic iodide (2 g.) and fractionally precipitating with dilute potassium iodide solution. The least soluble fractions of red plates and prisms of the lattice compound (*vide supra*) were replaced sharply by much lighter orange-red micaceous plates of the dextro iodide as the fractionation proceeded. An even sharper separation could be achieved by making the solution alkaline with caustic soda as soon as the plates of the dextro form appeared. In this way the antimonyl tartrate radicle was destroyed and only the least soluble dextro iodide precipitated.

The lattice compound was recrystallised either from water, potassium iodide solution or potassium antimonyl tartrate solution—the same substance always being obtained. The crystals became scarlet red in a desiccator or on warming, but regained their lighter colour on standing in moist air. The pure laevo iodide was obtained by solution in sodium hydroxide solution, followed by addition of potassium iodide.

The d and l iodides were crystallised several times from hot water and obtained finally in orange-red micaceous plates.

A 0·0408% solution of the lattice compound in water gave $\alpha_D^{20} = -0·47°$ (2 dm. tube), whence $[\alpha]_D^{20} = -576°$.

A 0·040% solution of the laevo iodide in water in a 2 dm. tube gave $\alpha_D^{20} = -0·65^{6°}$ and $\alpha_{5461}^{20} = -0·62°$, whence $[\alpha]_D^{20} = -819°$ and $[\alpha]_{5461}^{20} = -775°$.

A 0·040% solution of the dextro iodide in water gave $\alpha_D^{20} = +0·65^{6°}$ and $\alpha_{5461}^{20} = +0·62°$, $[\alpha] = +820°$ and $[\alpha]_{5461}^{20} = +775°$.

Analytical Data.

Found : I = 7·4% ; Sb = 14·05% ; N = 7·34%.

Calculated for $2Ru(C_{10}H_8N_2)_3(SbO.C_4H_4O_6)_2.Ru(C_{10}H_8N_2)_3I_2.18H_2O$: I = 7·35% ; Sb = 14·18% ; N = 7·34%.

Found, for d form : Ru = 11·60%. Calculated for $Ru(C_{10}H_8N_2)_3I_2.3H_2O$: Ru = 11·56%.

The Oxidation of d and l Tris-Dipyridyl Ruthenium III Iodides.

Solutions of the d and l iodides (0·02%) in 1 N sulphuric acid were oxidised with solid ceric ammonium nitrate. The orange solutions first became brown due to the liberation of iodine, which was then further oxidised to iodate and then blue coloured due to the $Ru(dipy)_3^{+++}$ ion. The oxidised solutions were immediately examined for rotation.

l form (oxidised) $\alpha_D^{20} = +0·11°$ (2 dm. tube), $\alpha_{5461}^{20} = +0·08°$ (2 dm. tube)

d form (oxidised) $\alpha_D^{20} = -0·12°$ (2 dm. tube), $\alpha_{5461}^{20} = -0·07°$ (2 dm. tube).

The specific rotations of the oxidised solutions for the ion $Ru(dipy)_3^{+++}$ compared with the ion $Ru(dipy)_3^{++}$ are shown in the table below.

Ion.	$[\alpha]_D^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{5791}^{25}$ *
d Ru(dipy)$_3$$^{+++}$ (by oxidation of l Ru(dipy)$^{++}$)	+426°	+310°	—
l Ru(dipy)$^{+++}$ (by oxidation of d Ru(dipy)$_3$$^{++}$)	—465°	—271°	—
d Ru(dipy)$_3$$^{++}$	+1269°	+1200°	+1264°
l Ru(dipy)$_3$$^{++}$	—1270°	—1200°	—1198°

* Calculated from Burstall (*loc. cit.*).

After the rotations were determined the solutions were reduced by the careful addition of ferrous sulphate crystals, and the original ruthenium II complex was regenerated with its rotation unchanged in each instance. During the time of the measurement, therefore, racemisation had not occurred.

SUMMARY.

Tris-dipyridyl ruthenium II iodide has been resolved through the curious lattice compound {2Ru(dipy)$_3$(SbO.Tart)$_2$.Ru(dipy)$_3$I$_2$}18H$_2$O. The d and l forms when oxidised with ceric nitrate underwent inversion of the sign of the rotation for both the Na$_D$ and Hg$_{5461}$ lines due to the change in the absorption spectrum in passing from the ion Ru(dipy)$_3$$^{++}$ to Ru(dipy)$_3$$^{+++}$, and the original rotation was regained in sign and magnitude on reduction.

ACKNOWLEDGEMENTS.

REFERENCES.

Burstall, 1936. *J. Chem. Soc.*, 172.
Dwyer, 1949. THIS JOURNAL, 83, 134.
Dwyer and Gyarfas, 1949. *Nature*, 163, 918.
————————— 1949. THIS JOURNAL, 83, 134.

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COMPLEX COMPOUNDS OF AUROUS HALIDES AND AUROUS CYANIDE WITH DIPHENYLMETHYL AND DIMETHYLPHENYL ARSINE.

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The tertiary aliphatic arsine and phosphine complexes of cuprous, argentous and aurous halides have been described by Mann and Purdie (1936), who found that one molecule of arsine or phosphine was coordinated with the metallic halide. The cuprous and argentous complexes were found to be tetrameric whilst the gold complex was monomeric. The structure of tetrakis monoiodo triethylarsine copper I investigated by crystal structure analysis (Mann, Purdie and Wells, 1937*a*) showed that in the macro molecule each copper atom was tetrahedral by reason of iodine bridges, whilst each iodine atom was three covalent. The stability of the silver compound $[Ag.IAs(C_2H_5)_2]_4$ was much lower than the copper compound, and in solution extensive dissociation to the two covalent monomeric form occurred. Burrows and Parker (1933) found that the silver halide complexes with diphenylmethyl arsine and dimethyl-phenylarsine were highly insoluble, and of the form $Ag(Ph_2MeAs)_2.X$. With boiling alcohol decomposition occurred with loss of arsine, but evidence was not found for the existence of complexes with only one molecule of arsine coordinated. Recent reinvestigation of these compounds (Dwyer and Savage, 1949) under a variety of conditions also failed to isolate compounds containing only one molecule of arsine. Since the insolubility of the compounds precluded molecular weight determinations, it is not possible to know whether the bis-arsine complexes are polymeric and contain four-covalent silver or are monomeric with the silver atom three-covalent. It is significant that Burrows and Sandford (1936), operating with the same two arsines, were able to isolate cuprous halide complexes which contained only one molecule of the arsine and were monomeric, suggesting that the type of arsine coordinated has some influence on the possibility of polymeric molecules.

The aurous halide complexes with tertiary arsines and phosphines were thoroughly studied by Mann and Purdie and Wells (1937*b*) and were found to be monomeric, of the type $R_3As.Aux$ ($R=C_2H_5$, C_3H_7, C_4H_9; $X=Cl$, Br, I, CNS) and contained two covalent gold. Many of these compounds were notably stable, and could be distilled under vacuum.

In the present investigation it was thought valuable to determine whether the arsines used by Burrows and Sandford (*loc. cit.*) would yield the usual kind of gold complex, and whether a greater tendency to polymerisation would occur in the iodo than in the chloro compounds. The aurous chloride complexes were made by allowing two molecules of the arsine to react with one molecule of auric chloride in warm aqueous alcoholic solution when reduction and complex formation occurred rapidly.

$$AuCl_3 + R_3As + H_2O \rightarrow AuCl + R_3AsO + 2HCl$$

$$AuCl + R_3As \rightarrow R_3As.AuCl.$$

The bromo and iodo compounds were obtained by treatment of the chloro compound with potassium bromide and iodide.

The complexes after crystallisation from aqueous alcohol were obtained as fine white needles, with sharp melting points. Dilute solutions in benzene were monomeric and hence contained two-covalent gold, but the iodide showed a pronounced tendency towards association in concentrated solution. A $2\cdot5\%$ solution had almost doubled the calculated molecular weight and, if it is assumed that tetrameric molecules were formed, was nearly 40% associated into these macro molecules. It is evident that the stronger bonding power of the iodine atom has an important influence on the formation of associated molecules of the type described for the copper and silver complexes.

The coordination compounds of gold I, silver I and Copper I cyanides do not appear to have been investigated hitherto. They should be of special interest because of the linear –CN– bonds on the one hand and the high bonding power of the CN group on the other. Whilst silver and cuprous cyanide both dissolve in alcoholic solutions of tertiary arsines, and complex compounds are precipitated on dilution with water or evaporation of the solvent, they lose arsine so easily that they cannot be purified and ultimately decompose completely to the original cyanide (Dwyer and Savage, *loc. cit.*). With aurous cyanide and diphenyl methyl arsine two impure compounds could be obtained : $AuCN.2Ph_2MeAs$ I and $AuCN.Ph_2MeAs$ II. The corresponding compounds with dimethyl phenyl arsine were obtained only as sticky gums and have not been investigated further.

The bis arsine complex I was obtained as a white crystalline substance, easily soluble in organic solvents to colourless solutions, which became yellow on standing or warming and deposited the monoarsine complex II as a pale yellow powder. In freezing bromoform I was dissociated to give a molecular weight almost half of the calculated value. One molecule of arsine was dissociated from the compound and could be easily detected by its odour. The compound I is considered to contain three-covalent gold. It is probable that the silver halide complexes containing two molecules of arsine described by Burrows and Parker (*loc. cit.*) are also three-covalent. It is significant that deposition of the yellow substance II did not occur except on warming, so that apparently a soluble two-covalent complex $AuCN.Ph_2MeAs$ may exist in solution as an unstable compound. With excess arsine this compound apparently passes into I or alternatively passes into the yellow substance II, which from its insolubility in all solvents, including boiling nitrobenzene, is considered to be polymeric.

The substance II is formulated as containing three-covalent gold through an infinite chain of –Au–CN–Au–CN– groups. The ease of transformation of II into I by treatment with excess arsine, and the loss of arsine from II by continued boiling with organic solvents to yield almost pure aurous cyanide are consistent with this formulation.

$$- - CN——Au——CN——Au——CN——Au- - -$$
$$\qquad\quad |\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$\qquad\quad AsR_3\qquad\qquad AsR_3\qquad\qquad AsR_3$$
$$\qquad\qquad\qquad\qquad II$$

An investigation is now being made of the aurous, cuprous and silver halide and cyanide complexes with diarsines such as ethylene bis-diphenyl arsine and ethylene bis phenylmethyl arsine, which should provide further evidence of the existence of three covalent complexes of these metals.

EXPERIMENTAL.

Auric chloride solution (50 mls.—1% with respect to Au) was mixed with alcohol (20 mls.) and heated to 50° C. The arsine (2 mols.) in alcohol (20 mls.) was added gradually to the warm gold solution with constant stirring. The yellow colour was soon discharged and a colourless

solution of the chloro complex resulted. The bromo or iodo complexes were formed by adding 5 mls. of 10% KBr or KI solution and keeping the solution warm for 10 minutes. Water was finally added until a permanent opalescence resulted—and the mixture allowed to cool slowly. The addition of a little petroleum ether dissolved traces of unreacted arsine and prevented the formation of gums or oils. The white crystalline products were crystallised from warm aqueous alcohol. The series prepared from PhMe$_2$As crystallised as needles, and from Ph$_2$MeAs as plates.

PhMe$_2$As.AuCl, m.p. 121° C.	Ph$_2$MeAs.AuCl, m.p. 121° C.
PhMe$_2$As.AuBr, m.p. 120·5° C.	Ph$_2$MeAs.AuBr, m.p. 118·5° C.
PhMe$_2$As.AuI, m.p. 130·5° C.	Ph$_2$MeAs.AuI, m.p. 128° C.

All were soluble in chloroform, benzene, acetone, sparingly soluble in petroleum ether and glacial acetic acid, and insoluble in water. Prolonged heating in any of these solvents led to decomposition and precipitation of gold. Dilute solutions in light became purple or brown, as do the crystals.

TABLE I.

Analytical Data.

Compound.	Au.		Halogen.		C.		H.	
	Found.	Cal-culated.	Found.	Cal-culated.	Found.	Cal-culated.	Found.	Cal-culated.
PhMe$_2$As.AuCl ..	48·5	47·65	8·63	8·56	22·96	23·15	2·80	2·65
PhMe$_2$As.AuBr ..	42·8	42·9	17·32	17·40	20·31	20·90	2·52	2·41
PhMe$_2$As.AuI ..	39·15	39·0	24·53	25·15	19·09	18·98	2·30	2·18
Ph$_2$MeAs.AuCl ..	41·0	41·4	7·53	7·45	32·85	32·75	2·87	2·72
Ph$_2$MeAs.AuBr ..	37·0	37·8	15·48	15·37	30·50	30·00	2·63	2·49
Ph$_2$MeAs.AuI ..	34·1	34·75	21·56	22·35	27·08	27·48	2·25	2·29

TABLE II.

Molecular Weights.

	PhMe$_2$As.AuI.			Ph$_2$MeAs.AuCl.		
Concentration	0·025 M	0·04 M	0·051 M	0·02 M	0·07 M	0·08 M
Molecular weight ..	602	652	756	451	504	543
Calculated molecular weight	—	506	—	—	477	—

I. Bis-diphenyl Methyl Arsine Gold I Cyanide.

Auric chloride solution (50 mls.—1% with respect to Au) was treated with diphenylmethyl arsine (1·85 g.—3 mols.) in alcohol (30 mls.) followed by potassium cyanide (0·17 g.) dissolved in water (10 mls.). Water was then added in excess and the resulting white oil became solid on shaking with petroleum ether. It was recrystallised from aqueous alcohol containing a little arsine and the white crystals washed with a little petroleum ether. This washing could not be carried to completion without decomposing the compound. The substance melted at 91° C. It was soluble in benzene, chloroform, alcohol and acetone, but on heating in any of these solvents decomposed with the separation of the yellow form. The solid was unstable and gradually became yellow with the development of the odour of arsine.

Found : Au=29·2%, 26·6% ; C=46·1% ; H=3·8%. Molecular weight in bromoform from ebullioscopic measurements : 376, 441, 516 for 0·018 M, 0·03 M, 0·04 M solutions, respectively.

Calculated for $AuCN.2(C_6H_5)_2CH_3As$: $Au = 27.73\%$; $C = 45.5\%$; $H = 3.68\%$. Molecular weight $= 712$.

II. Diphenylmethylarsine Gold I Cyanide.

This substance could be prepared like the compound above by using 2 mols. of arsine and warming the mixture or preferably by boiling I in benzene or alcohol solution. It could not be recrystallised, being insoluble in all solvents even in nitrobenzene. It dissolved in alcohol and arsine to form a colourless solution of I. On heating, the substance became viscous at about 85° C. and decomposed at about 280° C. The compound could not be obtained pure, as it appeared to be always contaminated with aurous cyanide. The latter substance could be isolated almost pure by very long boiling of II with bromobenzene.

Found : $Au = 84.46$, 84.42%. Calculated for $AuCN$: $Au = 84.43\%$.

Found : $Au = 45.2$, 46.7%. Calculated for $(AuCN.(C_6H_5)_2CH_3As)n$: $Au = 42.20\%$.

SUMMARY.

Aurous halides react with diphenylmethylarsine and dimethylphenylarsine to yield complexes of the type $AuX.AsR_3$. There is evidence of polymerisation of the iodo compound in concentrated solution—possibly due to the formation of tetrameric molecules. With aurous cyanide two complexes were obtained, a yellow, highly insoluble probably polymeric substance—$(AuCN.Ph_2MeAs)*$— and an unstable white substance containing two molecules of arsine in which the gold atom is three-covalent.

ACKNOWLEDGEMENTS.

REFERENCES.

Burrows and Parker, 1933. *J. Am. Chem. Soc.*, **55**, 4133.
Burrows and Sandford, 1936. THIS JOURNAL, **69**, 182.
Dwyer and Savage, 1949. Unpublished work.
Mann and Purdie, 1936. *J. Chem. Soc.*, 1503.
Mann, Purdie and Wells, 1937a. *Nature*, **140**, 502.
—— ——————————— 1937b. *J. Chem. Soc.*, 1828.

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KEPLER'S PROBLEM—THE PARABOLIC CASE.

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The solution of the parabolic case of Keplerian motion is given by

$$12\mu + \mu^3 = 12\sqrt{2}\,kq^{-3/2}t = D = 0 \cdot 29192930\,q^{-3/2}t$$

where, in the notation of a former paper (Wood, 1950), $\mu = 2\tan v/2$ and, with the constant given, t is in days. The solution of this equation is needed not only for the parabolic orbit but also to give a first approximation in the case of a nearly parabolic ellipse or hyperbola.

In order to disclose the range of variables for which solution is commonly necessary an examination was made of the orbits which do occur. The lists of comet orbits of Galle (1894), Chambers (1889 and 1909), Winlock (1896) and Crommelin (1925 and 1932) and the comet notes of current journals for 1931 to 1940 were examined.

Any tabulation naturally proceeds from perihelion ($t = 0$) and carries on as far as the computer may think desirable. Two of the most convenient existing tables, those of Strömgren (1927) and Subbotin (1929), give $\tan v/2$ with argument $B(=tq^{-3/2})$ as far as $B = 300$. From the above list those comets having parabolic or nearly parabolic orbits were selected which had been observed in a part of their orbit for which $B > 300$. From this list was taken the only one (Halley's) for which the solution in the elliptical form becomes appropriate before B reaches 300—incidentally no comet with a hyperbolic orbit has been observed beyond the zone of applicability of the nearly parabolic solution. This left 36 comets for which a solution with $B > 300$ was necessary, the extreme value of B corresponding to any observation being 377,000 for comet 1882 II.

There is a strong tendency for the average period of observation of comets to increase. The following table gives the average duration of visibility of comets (omitting Halley's and Schwassmam—Wachmann 1925 II). During successive twenty-year periods.

Period.	Number of Comets.	Mean Duration of Visibility (in Days).
1851 to 1870	76	75
1871 to 1890	92	95
1891 to 1910	94	115
1911 to 1930	103	131

This tendency continues, due to the effort of several observer's, notably van Biesbroeck, to extend observed orbital arcs by the use of large telescopes.

The argument to be used for tables given here is D $(3 \cdot 42 \ldots D=B)$ and the values of D corresponding to greatest observed distances from perihelion of the comets in the period 1851-1940 are distributed as follows :

Max D.		Number of Comets.
100 to 200	..	14
200 to 400	..	6
400 to 1000	..	3
> 1000	..	7

If we try to relate the period of visibility of comets to the perihelion distance we find that for perihelion distances from 0 to about $1 \cdot 4$ units the average duration remains nearly constant at about 90 days but with q between $1 \cdot 6$ and $2 \cdot 0$ units they have an average period of visibility of about 250 days which thereafter falls off.

In the circumstances large values of D are very probable for comets of small perihelion distance and all of the comets in the above list having max $D > 100$ have q small. Although the existing tables cover the majority of cases and it would be impracticable to give full tabulation as far as the extreme case, it is nevertheless desirable to have convenient processes to deal with any case that may occur, especially in view of the increased capacity to observe comets at great distances.

Below are tabulated two methods of solving the parabolic equation. Table 1 was formed by calculating approximate values of μ at ten times the interval of the table (except for small portions where five times was necessary) using the tables of Oppolzer (1886). These were corrected by an iterative process to give values accurate to two places beyond what is given in Table 1, differenced and subtabulated to the interval of the table. It is intended that errors will not exceed $0 \cdot 52$ unit of the last recorded place.

The first part of Table 1 gives μ to seven decimal places at interval $0 \cdot 1$ of D up to 100 and the second part $(100 < D < 1000)$ at interval 1 gives μ to six decimals. The effect of the third difference being negligible throughout the table we may interpolate with the Newton-Gauss formula

$$\mu_n = (1-n)\mu_0 + n\mu_1 - \frac{n(1-n)}{2}\delta^2\mu_0$$

where n is the fraction of the interval to be interpolated. $\delta^2\mu$ is given in Table 1 where it is appreciable and when linear interpolation is possible the first difference is tabulated. The coefficient of the second difference is given in the Critical Table on the interleaved flap.

There are two points for comment about this table. It would have been possible to form a table at a closer interval not requiring the use of second differences ; but using a calculating machine with an easily accessible list of second difference coefficients involves very little more work (only a few seconds) than linear interpolation and the time for the determination of μ has already, by such a table as this, been reduced to only a small proportion of the time needed to produce one ephemeris place. The extra bulk of table required to avoid the use of second differences seems unjustifiable. Also, an argument much used in tables of parabolic motion is $tq^{-3/2}$, but, with $12\sqrt{2}kq^{-3/2}$ pre-computed for the orbit, the argument adopted here involves no extra time and

n	$\frac{n(1-n)}{2}$	n	n	$\frac{n(1-n)}{2}$	n	n	$\frac{n(1-n)}{2}$	n	n	$\frac{n(1-n)}{2}$	n
0.0000		1.0000	0.0675		0.9325	0.1492		0.8508	0.2571		0.7429
	0.000			0.032			0.064			0.096	
.0010		0.9990	.0698		.9302	.1521		.8479	.2612		.7388
	.001			.033			.065			.097	
.0030		.9970	.0722		.9278	.1550		.8450	.2654		.7346
	.002			.034			.066			.098	
.0050		.9950	.0745		.9255	.1579		.8421	.2697		.7303
	.003			.035			.067			.099	
.0070		.9930	.0769		.9231	.1608		.8392	.2741		.7259
	.004			.036			.068			.100	
.0090		.9910	.0792		.9208	.1638		.8362	.2786		.7214
	.005			.037			.069			.101	
.0111		.9889	.0816		.9184	.1668		.8332	.2832		.7168
	.006			.038			.070			.102	
.0131		.9869	.0840		.9160	.1698		.8302	.2878		.7122
	.007			.039			.071			.103	
.0152		.9848	.0864		.9136	.1728		.8272	.2926		.7074
	.008			.040			.072			.104	
.0172		.9828	.0889		.9111	.1759		.8241	.2975		.7025
	.009			.041			.073			.105	
.0193		.9807	.0913		.9087	.1790		.8210	.3025		.6975
	.010			.042			.074			.106	
.0214		.9786	.0937		.9063	.1821		.8179	.3076		.6924
	.011			.043			.075			.107	
.0235		.9765	.0962		.9038	.1853		.8147	.3129		.6871
	.012			.044			.076			.108	
.0256		.9744	.0987		.9013	.1885		.8115	.3183		.6817
	.013			.045			.077			.109	
.0277		.9723	.1012		.8988	.1917		.8083	.3239		.6761
	.014			.046			.078			.110	
.0298		.9702	.1037		.8963	.1950		.8050	.3297		.6703
	.015			.047			.079			.111	
.0320		.9680	.1062		.8938	.1983		.8017	.3356		.6644
	.016			.048			.080			.112	
.0341		.9659	.1088		.8912	.2016		.7984	.3418		.6582
	.017			.049			.081			.113	
.0363		.9637	.1114		.8886	.2050		.7950	.3483		.6517
	.018			.050			.082			.114	
.0384		.9616	.1139		.8861	.2084		.7916	.3550		.6450
	.019			.051			.083			.115	
.0406		.9594	.1165		.8835	.2119		.7881	.3621		.6379
	.020			.052			.084			.116	
.0428		.9572	.1192		.8808	.2153		.7847	.3696		.6304
	.021			.053			.085			.117	
.0450		.9550	.1218		.8782	.2189		.7811	.3775		.6225
	.022			.054			.086			.118	
.0472		.9528	.1245		.8755	.2225		.7775	.3859		.6141
	.023			.055			.087			.119	
.0494		.9506	.1271		.8729	.2261		.7739	.3951		.6049
	.024			.056			.088			.120	
.0516		.9484	.1298		.8702	.2298		.7702	.4051		.5949
	.025			.057			.089			.121	
.0539		.9461	.1325		.8675	.2335		.7665	.4163		.5837
	.026			.058			.090			.122	
.0561		.9439	.1353		.8647	.2373		.7627	.4292		.5708
	.027			.059			.091			.123	
.0584		.9416	.1380		.8620	.2411		.7589	.4452		.5548
	.028			.060			.092			.124	
.0606		.9394	.1408		.8592	.2450		.7550	.4683		.5317
	.029			.061			.093			.125	
.0629		.9371	.1436		.8564	.2490		.7510	.5316		.4684
	.030			.062			.094			.124	
.0652		.9348	.1464		.8536	.2530		.7470	.5547		.4453
	0.031			0.063			0.095			0.123	
0.0675		0.9325	0.1492		0.8508	0.2571		0.7429	0.5707		0.4293

In critical cases take the value of $n(1-n)/2$ lying higher on the page.

$$\mu_n = (1-n)\mu_0 + n\mu_1 - \frac{n(1-n)}{2}\delta^2\mu_0$$

$\delta^2\mu_0$ is always negative.

TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
0·0	0·000 0000	0	5·0	0·410 8859	125	10·0	0·791 9429	178	15·0	1·129 8170	171
0·1	0·008 3333	3	5·1	0·418 8755	129	10·1	0·799 1378	178	15·1	1·136 1258	171
0·2	0·016 6663	6	5·2	0·426 8522	129	10·2	0·806 3149	177	15·2	1·142 4175	169
0·3	0·024 9987	9	5·3	0·434 8160	132	10·3	0·813 4743	180	15·3	1·148 6923	170
0·4	0·033 3302	11	5·4	0·442 7666	133	10·4	0·820 6157	177	15·4	1·154 9501	169
0·5	0·041 6606	14	5·5	0·450 7039	135	10·5	0·827 7394	180	15·5	1·161 1910	169
0·6	0·049 9896	18	5·6	0·458 6277	136	10·6	0·834 8451	179	15·6	1·167 4150	168
0·7	0·058 3168	20	5·7	0·466 5379	139	10·7	0·841 9329	179	15·7	1·173 6222	168
0·8	0·066 6420	23	5·8	0·474 4342	139	10·8	0·849 0028	179	15·8	1·179 8126	167
0·9	0·074 9649	26	5·9	0·482 3166	142	10·9	0·856 0548	180	15·9	1·185 9863	167
1·0	0·083 2852	29	6·0	0·490 1848	142	11·0	0·863 0888	179	16·0	1·192 1433	166
1·1	0·091 6026	31	6·1	0·498 0388	145	11·1	0·870 1049	180	16·1	1·198 2837	166
1·2	0·099 9169	35	6·2	0·505 8783	146	11·2	0·877 1030	179	16·2	1·204 4075	165
1·3	0·108 2277	37	6·3	0·513 7032	147	11·3	0·884 0832	181	16·3	1·210 5148	165
1·4	0·116 5348	40	6·4	0·521 5134	149	11·4	0·891 0453	179	16·4	1·216 6056	165
1·5	0·124 8379	43	6·5	0·529 3087	149	11·5	0·897 9895	179	16·5	1·222 6799	163
1·6	0·133 1367	46	6·6	0·537 0891	152	11·6	0·904 9158	181	16·6	1·228 7379	163
1·7	0·141 4309	48	6·7	0·544 8543	153	11·7	0·911 8240	179	16·7	1·234 7796	163
1·8	0·149 7203	51	6·8	0·552 6042	153	11·8	0·918 7143	179	16·8	1·240 8050	162
1·9	0·158 0046	54	6·9	0·560 3388	156	11·9	0·925 5867	181	16·9	1·246 8142	162
2·0	0·166 2835	56	7·0	0·568 0578	156	12·0	0·932 4410	178	17·0	1·252 8072	161
2·1	0·174 5568	60	7·1	0·575 7612	157	12·1	0·939 2775	180	17·1	1·258 7841	160
2·2	0·182 8241	62	7·2	0·583 4489	159	12·2	0·946 0960	179	17·2	1·264 7450	161
2·3	0·191 0852	64	7·3	0·591 1207	159	12·3	0·952 8966	180	17·3	1·270 6898	159
2·4	0·199 3399	·67	7·4	0·598 7766	162	12·4	0·959 6792	178	17·4	1·276 6187	160
2·5	0·207 5879	70	7·5	0·606 4163	161	12·5	0·966 4440	179	17·5	1·282 5316	157
2·6	0·215 8289	73	7·6	0·614 0399	162	12·6	0·973 1909	179	17·6	1·288 4288	159
2·7	0·224 0626	75	7·7	0·621 6473	165	12·7	0·979 9199	178	17·7	1·294 3101	157
2·8	0·232 2888	77	7·8	0·629 2382	163	12·8	0·986 6311	179	17·8	1·300 1757	156
2·9	0·240 5073	80	7·9	0·636 8128	167	12·9	0·993 3244	177	17·9	1·306 0257	157
3·0	0·248 7178	82	8·0	0·644 3707	166	13·0	1·000 0000	178	18·0	1·311 8600	156
3·1	0·256 9201	85	8·1	0·651 9120	167	13·1	1·006 6578	178	18·1	1·317 6787	155
3·2	0·265 1139	88	8·2	0·659 4366	168	13·2	1·013 2978	177	18·2	1·323 4819	154
3·3	0·273 2989	90	8·3	0·666 9444	168	13·3	1·019 9201	177	18·3	1·329 2697	154
3·4	0·281 4749	91	8·4	0·674 4354	171	13·4	1·026 5247	177	18·4	1·335 0421	154
3·5	0·289 6418	95	8·5	0·681 9093	169	13·5	1·033 1116	176	18·5	1·340 7991	153
3·6	0·297 7992	97	8·6	0·689 3663	172	13·6	1·039 6809	176	18·6	1·346 5408	152
3·7	0·305 9469	99	8·7	0·696 8061	171	13·7	1·046 2326	176	18·7	1·352 2673	152
3·8	0·314 0847	102	8·8	0·704 2288	172	13·8	1·052 7667	176	18·8	1·357 9786	151
3·9	0·322 2123	103	8·9	0·711 6343	173	13·9	1·059 2832	175	18·9	1·363 6748	150
4·0	0·330 3296	106	9·0	0·719 0225	173	14·0	1·065 7822	174	19·0	1·369 3560	151
4·1	0·338 4363	108	9·1	0·726 3934	175	14·1	1·072 2638	175	19·1	1·375 0221	149
4·2	0·346 5322	110	9·2	0·733 7468	173	14·2	1·078 7279	175	19·2	1·380 6733	149
4·3	0·354 6171	112	9·3	0·741 0829	176	14·3	1·085 1745	173	19·3	1·386 3096	149
4·4	0·362 6908	114	9·4	0·748 4014	175	14·4	1·091 6038	173	19·4	1·391 9310	147
4·5	0·370 7531	117	9·5	0·755 7024	176	14·5	1·098 0158	173	19·5	1·397 5377	147
4·6	0·378 8037	118	9·6	0·762 9858	176	14·6	1·104 4105	173	19·6	1·403 1297	147
4·7	0·386 8425	120	9·7	0·770 2516	177	14·7	1·110 7879	172	19·7	1·408 7070	146
4·8	0·394 8693	123	9·8	0·777 4997	176	14·8	1·117 1481	172	19·8	1·414 2697	146
4·9	0·402 8838	124	9·9	0·784 7302	178	14·9	1·123 4911	171	19·9	1·419 8178	144
5·0	0·410 8859	125	10·0	0·791 9429	178	15·0	1·129 8170	171	20·0	1·425 3515	145

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TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
20·0	1·425 3515	145	25·0	1·684 8004	116	30·0	1·914 8811	95	35·0	2·121 2503	76
20·1	1·430 8707	144	25·1	1·689 6689	116	30·1	1·919 2241	93	35·1	2·125 1682	77
20·2	1·436 3755	142	25·2	1·694 5258	117	30·2	1·923 5578	95	35·2	2·129 0784	76
20·3	1·441 8661	144	25·3	1·699 3710	116	30·3	1·927 8820	92	35·3	2·132 9810	75
20·4	1·447 3423	141	25·4	1·704 2046	114	30·4	1·932 1970	93	35·4	2·136 8761	77
20·5	1·452 8044	142	25·5	1·709 0268	115	30·5	1·936 5027	93	35·5	2·140 7635	74
20·6	1·458 2523	141	25·6	1·713 8375	114	30·6	1·940 7991	91	35·6	2·144 6435	76
20·7	1·463 6861	141	25·7	1·718 6368	114	30·7	1·945 0864	93	35·7	2·148 5159	74
20·8	1·469 1058	139	25·8	1·723 4247	113	30·8	1·949 3644	90	35·8	2·152 3809	74
20·9	1·474 5116	139	25·9	1·728 2013	112	30·9	1·953 6334	92	35·9	2·156 2385	75
21·0	1·479 9035	139	26·0	1·732 9667	113	31·0	1·957 8932	90	36·0	2·160 0886	73
21·1	1·485 2815	138	26·1	1·737 7208	111	31·1	1·962 1440	90	36·1	2·163 9314	74
21·2	1·490 6457	137	26·2	1·742 4638	111	31·2	1·966 3858	90	36·2	2·167 7668 ,	73
21·3	1·495 9962	138	26·3	1·747 1957	111	31·3	1·970 6186	90	36·3	2·171 5949	72
21·4	1·501 3329	136	26·4	1·751 9165	110	31·4	1·974 8424	88	36·4	2·175 4158	74
21·5	1·506 6560	136	26·5	1·756 6263	110	31·5	1·979 0574	89	36·5	2·179 2293	71
21·6	1·511 9655	135	26·6	1·761 3251	109	31·6	1·983 2635	88	36·6	2·183 0357	73
21·7	1·517 2615	134	26·7	1·766 0130	109	31·7	1·987 4608	88	36·7	2·186 8348	72
21·8	1·522 5441	135	26·8	1·770 6900	109	31·8	1·991 6493	88	36·8	2·190 6267	71
21·9	1·527 8132	133	26·9	1·775 3561	107	31·9	1·995 8290	87	36·9	2·194 4115	71
22·0	1·533 0690	134	27·0	1·780 0115	107	32·0	2·000 0000	87	37·0	2·198 1892	71
22·1	1·538 3114	132	27·1	1·784 6562	108	32·1	2·004 1623	86	37·1	2·201 9598	70
22·2	1·543 5406	132	27·2	1·789 2901	105	32·2	2·008 3160	86	37·2	2·205 7234	71
22·3	1·548 7566	131	27·3	1·793 9135	107	32·3	2·012 4611	86	37·3	2·209 4799	70
22·4	1·553 9595	131	27·4	1·798 5262	106	32·4	2·016 5976	85	37·4	2·213 2294	70
22·5	1·559 1493	130	27·5	1·803 1283	104	32·5	2·020 7256	86	37·5	2·216 9719	70
22·6	1·564 3261	131	27·6	1·807 7200	105	32·6	2·024 8450	84	37·6	2·220 7074	68
22·7	1·569 4898	128	27·7	1·812 3012	105	32·7	2·028 9560	84	37·7	2·224 4361	70
22·8	1·574 6407	129	27·8	1·816 8719	103	32·8	2·033 0586	84	37·8	2·228 1578	68
22·9	1·579 7787	128	27·9	1·821 4323	103	32·9	2·037 1528	84	37·9	2·231 8727	69
23·0	1·584 9039	127	28·0	1·825 9824	104	33·0	2·041 2386	83	38·0	2·235 5807	68
23·1	1·590 0164	128	28·1	1·830 5221	101	33·1	2·045 3161	83	38·1	2·239 2819	68
23·2	1·595 1161	126	28·2	1·835 0517	103	33·2	2·049 3853	83	38·2	2·242 9763	68
23·3	1·600 2032	125	28·3	1·839 5710	101	33·3	2·053 4462	82	38·3	2·246 6639	67
23·4	1·605 2778	127	28·4	1·844 0802	101	33·4	2·057 4989	82	38·4	2·250 3448	67
23·5	1·610 3397	124	28·5	1·848 5793	101	33·5	2·061 5434	82	38·5	2·254 0190	67
23·6	1·615 3892	124	28·6	1·853 0683	100	33·6	2·065 5797	80	38·6	2·257 6865	67
23·7	1·620 4263	125	28·7	1·857 5473	100	33·7	2·069 6080	82	38·7	2·261 3473	66
23·8	1·625 4509	122	28·8	1·862 0163	100	33·8	2·073 6281	80	38·8	2·265 0015	67
23·9	1·630 4633	124	28·9	1·866 4753	98	33·9	2·077 6402	81	38·9	2·268 6490	65
24·0	1·635 4633	121	29·0	1·870 9245	99	34·0	2·081 6442	79	39·0	2·272 2900	65
24·1	1·640 4512	122	29·1	1·875 3638	98	34·1	2·085 6403	80	39·1	2·275 9245	67
24·2	1·645 4269	122	29·2	1·879 7933	98	34·2	2·089 6284	80	39·2	2·279 5523	64
24·3	1·650 3904	120	29·3	1·884 2130	97	34·3	2·093 6085	78	39·3	2·283 1737	65
24·4	1·655 3419	120	29·4	1·888 6230	97	34·4	2·097 5808	79	39·4	2·286 7886	65
24·5	1·660 2814	119	29·5	1·893 0233	96	34·5	2·101 5452	79	39·5	2·290 3970	64
24·6	1·665 2090	120	29·6	1·897 4140	96	34·6	2·105 5017	77	39·6	2·293 9990	65
24·7	1·670 1246	119	29·7	1·901 7951	96	34·7	2·109 4505	78	39·7	2·297 5945	63
24·8	1·675 0283	117	29·8	1·906 1666	95	34·8	2·113 3915	77	39·8	2·301 1837	64
24·9	1·679 9203	119	29·9	1·910 5286	95	34·9	2·117 3248	78	39·9	2·304 7665	63
25·0	1·684 8004	116	30·0	1·914 8811	95	35·0	2·121 2503	76	40·0	2·308 3430	64

TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
40·0	2·308 3430	64	45·0	2·479 5733	53	50·0	2·637 5754	45	55·0	2·784 4020	38
40·1	2·311 9131	62	45·1	2·482 8553	53	50·1	2·640 6154	44	55·1	2·787 2363	38
40·2	2·315 4770	63	45·2	2·486 1320	52	50·2	2·643 6510	44	55·2	2·790 0668	38
40·3	2·319 0346	63	45·3	2·489 4035	52	50·3	2·646 6822	45	55·3	2·792 8935	38
40·4	2·322 5859	62	45·4	2·492 6698	52	50·4	2·649 7089	43	55·4	2·795 7164	38
40·5	2·326 1310	62	45·5	2·495 9309	52	50·5	2·652 7313	45	55·5	2·798 5355	37
40·6	2·329 6699	62	45·6	2·499 1868	51	50·6	2·655 7492	43	55·6	2·801 3509	37
40·7	2·333 2026	61	45·7	2·502 4376	52	50·7	2·658 7628	43	55·7	2·804 1626	38
40·8	2·336 7292	62	45·8	2·505 6832	52	50·8	2·661 7720	43	55·8	2·806 9705	37
40·9	2·340 2496	61	45·9	2·508 9236	50	50·9	2·664 7769	43	55·9	2·809 7747	37
41·0	2·343 7639	60	46·0	2·512 1590	51	51·0	2·667 7775	44	56·0	2·812 5752	38
41·1	2·347 2722	62	46·1	2·515 3893	51	51·1	2·670 7737	42	56·1	2·815 3719	36
41·2	2·350 7743	59	46·2	2·518 6145	51	51·2	2·673 7657	44	56·2	2·818 1650	36
41·3	2·354 2705	61	46·3	2·521 8346	50	51·3	2·676 7533	42	56·3	2·820 9545	38
41·4	2·357 7606	60	46·4	2·525 0497	50	51·4	2·679 7367	43	56·4	2·823 7402	36
41·5	2·361 2447	60	46·5	2·528 2598	51	51·5	2·682 7158	42	56·5	2·826 5223	36
41·6	2·364 7228	59	46·6	2·531 4648	49	51·6	2·685 6907	42	56·6	2·829 3008	37
41·7	2·368 1950	60	46·7	2·534 6649	50	51·7	2·688 6614	43	56·7	2·832 0756	36
41·8	2·371 6612	58	46·8	2·537 8600	49	51·8	2·691 6278	42	56·8	2·834 8468	36
41·9	2·375 1216	60	46·9	2·541 0502	50	51·9	2·694 5900	42	56·9	2·837 6144	37
42·0	2·378 5760	58	47·0	2·544 2354	49	52·0	2·697 5480	41	57·0	2·840 3783	35
42·1	2·382 0246	59	47·1	2·547 4157	50	52·1	2·700 5019	43	57·1	2·843 1387	36
42·2	2·385 4673	58	47·2	2·550 5910	48	52·2	2·703 4515	40	57·2	2·845 8955	35
42·3	2·388 9042	58	47·3	2·553 7615	48	52·3	2·706 3971	43	57·3	2·848 6488	36
42·4	2·392 3353	58	47·4	2·556 9272	50	52·4	2·709 3384	40	57·4	2·851 3985	36
42·5	2·395 7606	57	47·5	2·560 0879	47	52·5	2·712 2757	42	57·5	2·854 1446	35
42·6	2·399 1802	58	47·6	2·563 2439	49	52·6	2·715 2088	40	57·6	2·856 8872	36
42·7	2·402 5940	57	47·7	2·566 3950	48	52·7	2·718 1379	42	57·7	2·859 6262	34
42·8	2·406 0021	57	47·8	2·569 5413	48	52·8	2·721 0628	40	57·8	2·862 3618	36
42·9	2·409 4045	57	47·9	2·572 6828	48	52·9	2·723 9837	41	57·9	2·865 0938	35
43·0	2·412 8012	57	48·0	2·575 8195	47	53·0	2·726 9005	41	58·0	2·867 8223	34
43·1	2·416 1922	56	48·1	2·578 9515	48	53·1	2·729 8132	40	58·1	2·870 5474	36
43·2	2·419 5776	56	48·2	2·582 0787	47	53·2	2·732 7219	40	58·2	2·873 2689	34
43·3	2·422 9574	56	48·3	2·585 2012	47	53·3	2·735 6266	40	58·3	2·875 9870	34
43·4	2·426 3316	56	48·4	2·588 3190	47	53·4	2·738 5273	40	58·4	2·878 7017	35
43·5	2·429 7002	55	48·5	2·591 4321	47	53·5	2·741 4240	41	58·5	2·881 4129	35
43·6	2·433 0633	56	48·6	2·594 5405	46	53·6	2·744 3166	38	58·6	2·884 1206	34
43·7	2·436 4208	55	48·7	2·597 6443	47	53·7	2·747 2054	41	58·7	2·886 8249	34
43·8	2·439 7728	55	48·8	2·600 7434	47	53·8	2·750 0901	39	58·8	2·889 5258	34
43·9	2·443 1193	55	48·9	2·603 8378	45	53·9	2·752 9709	40	58·9	2·892 2233	34
44·0	2·446 4603	54	49·0	2·606 9277	47	54·0	2·755 8477	39	59·0	2·894 9174	34
44·1	2·449 7959	55	49·1	2·610 0129	45	54·1	2·758 7206	39	59·1	2·897 6081	34
44·2	2·453 1260	54	49·2	2·613 0936	46	54·2	2·761 5896	39	59·2	2·900 2954	33
44·3	2·456 4507	54	49·3	2·616 1697	46	54·3	2·764 4547	39	59·3	2·902 9794	34
44·4	2·459 7700	54	49·4	2·619 2412	45	54·4	2·767 3159	39	59·4	2·905 6600	34
44·5	2·463 0839	54	49·5	2·622 3082	46	54·5	2·770 1732	38	59·5	2·908 3372	33
44·6	2·466 3924	53	49·6	2·625 3706	45	54·6	2·773 0267	39	59·6	2·911 0111	33
44·7	2·469 6956	53	49·7	2·628 4285	44	54·7	2·775 8763	39	59·7	2·913 6817	34
44·8	2·472 9935	54	49·8	2·631 4820	46	54·8	2·778 7220	38	59·8	2·916 3489	33
44·9	2·476 2860	52	49·9	2·634 5309	44	54·9	2·781 5639	38	59·9	2·919 0128	32
45·0	2·479 5733	53	50·0	2·637 5754	45	55·0	2·784 4020	38	60·0	2·921 6735	34

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TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
60·0	2·921 6735	34	65·0	3·050 6859	30	70·0	3·172 4896	26	75·0	3·287 9463	21
60·1	2·924 3308	33	65·1	3·053 1894	28	70·1	3·174 8583	25	75·1	3·290 1959	24
60·2	2·926 9848	32	65·2	3·055 6901	28	70·2	3·177 2245	25	75·2	3·292 4431	21
60·3	2·929 6356	33	65·3	3·058 1880	30	70·3	3·179 5882	25	75·3	3·294 6882	23
60·4	2·932 2831	33	65·4	3·060 6829	27	70·4	3·181 9494	25	75·4	3·296 9310	22
60·5	2·934 9273	32	65·5	3·063 1751	29	70·5	3·184 3081	26	75·5	3·299 1716	23
60·6	2·937 5683	33	65·6	3·065 6644	29	70·6	3·186 6642	24	75·6	3·301 4099	22
60·7	2·940 2060	31	65·7	3·068 1508	27	70·7	3·189 0179	26	75·7	3·303 6460	21
60·8	2·942 8406	33	65·8	3·070 6345	29	70·8	3·191 3690	24	75·8	3·305 8800	23
60·9	2·945 4719	33	65·9	3·073 1153	28	70·9	3·193 7177	25	75·9	3·308 1117	22
61·0	2·948 0999	31	66·0	3·075 5933	28	71·0	3·196 0639	24	76·0	3·310 3412	22
61·1	2·950 7248	32	66·1	3·078 0685	28	71·1	3·198 4077	26	76·1	3·312 5685	22
61·2	2·953 3465	32	66·2	3·080 5409	28	71·2	3·200 7489	25	76·2	3·314 7936	22
61·3	2·955 9650	32	66·3	3·083 0105	27	71·3	3·203 0877	24	76·3	3·317 0165	21
61·4	2·958 5803	32	66·4	3·085 4774	28	71·4	3·205 4241	25	76·4	3·319 2373	23
61·5	2·961 1924	31	66·5	3·087 9415	28	71·5	3·207 7580	24	76·5	3·321 4558	21
61·6	2·963 8014	32	66·6	3·090 4028	28	71·6	3·210 0895	24	76·6	3·323 6722	21
61·7	2·966 4072	31	66·7	3·092 8613	27	71·7	3·212 4185	24	76·7	3·325 8865	23
61·8	2·969 0099	31	66·8	3·095 3171	28	71·8	3·214 7451	25	76·8	3·328 0985	21
61·9	2·971 6095	32	66·9	3·097 7701	27	71·9	3·217 0692	23	76·9	3·330 3084	21
62·0	2·974 2059	31	67·0	3·100 2204	27	72·0	3·219 3910	25	77·0	3·332 5162	22
62·1	2·976 7992	31	67·1	3·102 6680	28	72·1	3·221 7103	24	77·1	3·334 7218	21
62·2	2·979 3894	31	67·2	3·105 1128	26	72·2	3·224 0272	23	77·2	3·336 9253	22
62·3	2·981 9765	31	67·3	3·107 5550	28	72·3	3·226 3418	25	77·3	3·339 1266	21
62·4	2·984 5605	31	67·4	3·109 9944	27	72·4	3·228 6539	24	77·4	3·341 3258	22
62·5	2·987 1414	31	67·5	3·112 4311	27	72·5	3·230 9636	23	77·5	3·343 5228	20
62·6	2·989 7192	30	67·6	3·114 8651	27	72·6	3·233 2710	24	77·6	3·345 7178	22
62·7	2·992 2940	31	67·7	3·117 2964	26	72·7	3·235 5760	24	77·7	3·347 9106	21
62·8	2·994 8657	30	67·8	3·119 7251	28	72·8	3·237 8786	24	77·8	3·350 1013	21
62·9	2·997 4344	31	67·9	3·122 1510	26	72·9	3·240 1788	24	77·9	3·352 2899	22
63·0	3·000 0000	30	68·0	3·124 5743	27	73·0	3·242 4766	22	78·0	3·354 4763	20
63·1	3·002 5626	30	68·1	3·126 9949	26	73·1	3·244 7722	25	78·1	3·356 6607	21
63·2	3·005 1221	29	68·2	3·129 4129	27	73·2	3·247 0653	23	78·2	3·358 8430	21
63·3	3·007 6787	31	68·3	3·131 8282	26	73·3	3·249 3561	23	78·3	3·361 0232	21
63·4	3·010 2322	29	68·4	3·134 2409	27	73·4	3·251 6446	24	78·4	3·363 2013	21
63·5	3·012 7828	31	68·5	3·136 6509	25	73·5	3·253 9307	22	78·5	3·365 3773	20
63·6	3·015 3303	30	68·6	3·139 0584	28	73·6	3·256 2146	25	78·6	3·367 5513	21
63·7	3·017 8748	29	68·7	3·141 4631	25	73·7	3·258 4960	22	78·7	3·369 7232	21
63·8	3·020 4164	30	68·8	3·143 8653	26	73·8	3·260 7752	23	78·8	3·371 8930	21
63·9	3·022 9550	29	68·9	3·146 2649	27	73·9	3·263 0521	24	78·9	3·374 0607	20
64·0	3·025 4907	31	69·0	3·148 6618	25	74·0	3·265 3266	23	79·0	3·376 2264	21
64·1	3·028 0233	28	69·1	3·151 0562	26	74·1	3·267 5988	22	79·1	3·378 3900	20
64·2	3·030 5531	30	69·2	3·153 4480	27	74·2	3·269 8688	23	79·2	3·380 5516	21
64·3	3·033 0799	30	69·3	3·155 8371	25	74·3	3·272 1365	24	79·3	3·382 7111	20
64·4	3·035 6037	28	69·4	3·158 2237	25	74·4	3·274 4018	22	79·4	3·384 8686	20
64·5	3·038 1247	30	69·5	3·160 6078	27	74·5	3·276 6649	23	79·5	3·387 0241	21
64·6	3·040 6427	28	69·6	3·162 9892	24	74·6	3·278 9257	22	79·6	3·389 1775	20
64·7	3·043 1579	30	69·7	3·165 3682	27	74·7	3·281 1843	23	79·7	3·391 3289	20
64·8	3·045 6701	29	69·8	3·167 7445	25	74·8	3·283 4406	23	79·8	3·393 4783	21
64·9	3·048 1794	28	69·9	3·170 1183	25	74·9	3·285 6946	23	79·9	3·395 6256	19
65·0	3·050 6859	30	70·0	3·172 4896	26	75·0	3·287 9463	21	80·0	3·397 7710	21

TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
80·0	3·397 7710	21	85·0	3·502 5627	18	90·0	3·602 8285	17	95·0	3·699 0011	14
80·1	3·399 9143	20	85·1	3·504 6108	18	90·1	3·604 7907	16	95·1	3·700 8855	16
80·2	3·402 0556	19	85·2	3·506 6571	18	90·2	3·606 7513	16	95·2	3·702 7683	14
80·3	3·404 1950	21	85·3	3·508 7016	18	90·3	3·608 7103	17	95·3	3·704 6497	15
80·4	3·406 3323	20	85·4	3·510 7443	17	90·4	3·610 6676	15	95·4	3·706 5296	15
80·5	3·408 4676	19	85·5	3·512 7853	19	90·5	3·612 6234	17	95·5	3·708 4080	14
80·6	3·410 6010	21	85·6	3·514 8244	18	90·6	3·614 5775	16	95·6	3·710 2850	15
80·7	3·412 7323	19	85·7	3·516 8617	17	90·7	3·616 5300	17	95·7	3·712 1605	15
80·8	3·414 8617	20	85·8	3·518 8973	18	90·8	3·618 4808	15	95·8	3·714 0345	14
80·9	3·416 9891	20	85·9	3·520 9311	18	90·9	3·620 4301	16	95·9	3·715 9071	16
81·0	3·419 1145	19	86·0	3·522 9631	18	91·0	3·622 3778	17	96·0	3·717 7781	13
81·1	3·421 2380	20	86·1	3·524 9933	17	91·1	3·624 3238	15	96·1	3·719 6478	15
81·2	3·423 3595	20	86·2	3·527 0218	18	91·2	3·626 2683	17	96·2	3·721 5160	15
81·3	3·425 4790	17	86·3	3·529 0485	17	91·3	3·628 2111	15	96·3	3·723 3827	15
81·4	3·427 5966	19	86·4	3·531 0735	18	91·4	3·630 1524	16	96·4	3·725 2479	13
81·5	3·429 7123	20	86·5	3·533 0967	18	91·5	3·632 0921	17	96·5	3·727 1118	16
81·6	3·431 8260	20	86·6	3·535 1181	17	91·6	3·634 0301	15	96·6	3·728 9741	13
81·7	3·433 9377	19	86·7	3·537 1378	18	91·7	3·635 9666	15	96·7	3·730 8351	15
81·8	3·436 0475	19	86·8	3·539 1557	17	91·8	3·637 9016	17	96·8	3·732 6946	15
81·9	3·438 1554	19	86·9	3·541 1719	17	91·9	3·639 8349	16	96·9	3·734 5526	14
82·0	3·440 2614	20	87·0	3·543 1864	18	92·0	3·641 7666	15	97·0	3·736 4092	14
82·1	3·442 3654	19	87·1	3·545 1991	17	92·1	3·643 6968	16	97·1	3·738 2644	14
82·2	3·444 4675	19	87·2	3·547 2101	17	92·2	3·645 6254	15	97·2	3·740 1182	15
82·3	3·446 5677	19	87·3	3·549 2194	18	92·3	3·647 5525	16	97·3	3·741 9705	14
82·4	3·448 6660	20	87·4	3·551 2269	17	92·4	3·649 4780	16	97·4	3·743 8214	14
82·5	3·450 7623	18	87·5	3·553 2327	17	92·5	3·651 4019	15	97·5	3·745 6709	15
82·6	3·452 8568	19	87·6	3·555 2368	17	92·6	3·653 3243	16	97·6	3·747 5189	14
82·7	3·454 9494	20	87·7	3·557 2392	17	92·7	3·655 2451	16	97·7	3·749 3655	13
82·8	3·457 0400	18	87·8	3·559 2399	18	92·8	3·657 1643	15	97·8	3·751 2108	15
82·9	3·459 1288	19	87·9	3·561 2388	16	92·9	3·659 0820	15	97·9	3·753 0546	14
83·0	3·461 2157	19	88·0	3·563 2361	17	93·0	3·660 9982	16	98·0	3·754 8970	14
83·1	3·463 3007	19	88·1	3·565 2317	18	93·1	3·662 9128	15	98·1	3·756 7380	14
83·2	3·465 3838	18	88·2	3·567 2255	16	93·2	3·664 8259	16	98·2	3·758 5776	15
83·3	3·467 4650	18	88·3	3·569 2177	17	93·3	3·666 7374	15	98·3	3·760 4157	13
83·4	3·469 5444	19	88·4	3·571 2082	18	93·4	3·668 6474	15	98·4	3·762 2525	14
83·5	3·471 6219	19	88·5	3·573 1969	16	93·5	3·670 5559	16	98·5	3·764 0879	14
83·6	3·473 6975	18	88·6	3·575 1840	16	93·6	3·672 4629	16	98·6	3·765 9219	14
83·7	3·475 7713	19	88·7	3·577 1695	16	93·7	3·674 3683	15	98·7	3·767 7545	14
83·8	3·477 8432	18	88·8	3·579 1532	16	93·8	3·676 2722	16	98·8	3·769 5857	13
83·9	3·479 9133	19	88·9	3·581 1353	17	93·9	3·678 1745	14	98·9	3·771 4156	15
84·0	3·481 9815	19	89·0	3·583 1157	17	94·0	3·680 0754	16	99·0	3·773 2440	13
84·1	3·484 0478	17	89·1	3·585 0944	16	94·1	3·681 9747	14	99·1	3·775 0711	15
84·2	3·486 1124	20	89·2	3·587 0715	17	94·2	3·683 8726	16	99·2	3·776 8967	13
84·3	3·488 1750	17	89·3	3·589 0469	17	94·3	3·685 7689	15	99·3	3·778 7210	13
84·4	3·490 2359	19	89·4	3·591 0206	16	94·4	3·687 6637	15	99·4	3·780 5440	15
84·5	3·492 2949	18	89·5	3·592 9927	16	94·5	3·689 5570	15	99·5	3·782 3655	13
84·6	3·494 3521	18	89·6	3·594 9632	17	94·6	3·691 4488	15	99·6	3·784 1857	14
84·7	3·496 4075	19	89·7	3·596 9320	17	94·7	3·693 3391	14	99·7	3·786 0045	13
84·8	3·498 4610	17	89·8	3·598 8991	16	94·8	3·695 2280	15	99·8	3·787 8220	14
84·9	3·500 5128	19	89·9	3·600 8646	16	94·9	3·697 1153	15	99·9	3·789 6381	14
85·0	3·502 5627	18	90·0	3·602 8285	17	95·0	3·699 0011	14	100·0	3·791 4528	14

TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
100	3·791 453	136	150	4·566 193	66	200	5·167 521	39	250	5·667 009	28
101	3·809 526	134	151	4·579 574	65	201	5·178 358	39	251	5·676 225	26
102	3·827 465	130	152	4·592 890	66	202	5·189 156	40	252	5·685 415	27
103	3·845 274	130	153	4·606 140	63	203	5·199 914	38	253	5·694 578	25
104	3·862 953	126	154	4·619 327	63	204	5·210 634	38	254	5·703 716	27
105	3·880 506	125	155	4·632 451	62	205	5·221 316	39	255	5·712 827	25
106	3·897 934	122	156	4·645 513	62	206	5·231 959	37	256	5·721 913	26
107	3·915 240	121	157	4·658 513	61	207	5·242 565	37	257	5·730 973	26
108	3·932 425	118	158	4·671 452	61	208	5·253 134	38	258	5·740 007	25
109	3·949 492	117	159	4·684 330	59	209	5·263 665	36	259	5·749 016	25
110	3·966 442	115	160	4·697 149	59	210	5·274 160	36	260	5·758 000	25
111	3·983 277	112	161	4·709 909	58	211	5·284 619	37	261	5·766 959	24
112	4·000 000	112	162	4·722 611	58	212	5·295 041	35	262	5·775 894	26
113	4·016 611	109	163	4·735 255	57	213	5·305 428	36	263	5·784 803	·23
114	4·033 113	107	164	4·747 842	56	214	5·315 779	35	264	5·793 689	26
115	4·049 508	107	165	4·760 373	56	215	5·326 095	35	265	5·802 549	23
116	4·065 796	104	166	4·772 848	56	216	5·336 376	35	266	5·811 386	24
117	4·081 980	103	167	4·785 267	54	217	5·346 622	34	267	5·820 199	24
118	4·098 061	101	168	4·797 632	54	218	5·356 834	33	268	5·828 988	23
119	4·114 041	100	169	4·809 943	54	219	5·367 013	35	269	5·837 754	24
120	4·129 921	98	170	4·822 200	52	220	5·377 157	33	270	5·846 496	24
121	4·145 703	98	171	4·834 405	53	221	5·387 268	34	271	5·855 214	22
122	4·161 387	94	172	4·846 557	52	222	5·397 345	32	272	5·863 910	24
123	4·176 977	95	173	4·858 657	51	223	5·407 390	34	273	5·872 582	23
124	4·192 472	92	174	4·870 706	51	224	5·417 401	31	274	5·881 231	22
125	4·207 875	92	175	4·882 704	50	225	5·427 381	33	275	5·889 858	23
126	4·223 186	90	176	4·894 652	50	226	5·437 328	32	276	5·898 462	22
127	4·238 407	89	177	4·906 550	50	227	5·447 243	31	277	5·907 044	23
128	4·253 539	88	178	4·918 398	48	228	5·457 127	32	278	5·915 603	22
129	4·268 583	86	179	4·930 198	48	229	5·466 979	32	279	5·924 140	21
130	4·283 541	85	180	4·941 950	48	230	5·476 799	30	280	5·932 656	23
131	4·298 414	85	181	4·953 654	48	231	5·486 589	31	281	5·941 149	22
132	4·313 202	82	182	4·965 310	46	232	5·496 348	30	282	5·949 620	21
133	4·327 908	83	183	4·976 920	47	233	5·506 077	31	283	5·958 070	21
134	4·342 531	80	184	4·988 483	46	234	5·515 775	30	284	5·966 499	22
135	4·357 074	80	185	5·000 000	45	235	5·525 443	29	285	5·974 906	21
136	4·371 537	78	186	5·011 472	46	236	5·535 082	30	286	5·983 292	22
137	4·385 922	70	187	5·022 898	44	237	5·544 691	30	287	5·991 656	20
138	4·400 228	76	188	5·034 280	45	238	5·554 270	29	288	6·000 000	21
139	4·414 458	75	189	5·045 617	43	239	5·563 820	28	289	6·008 323	21
140	4·428 613	76	190	5·056 911	44	240	5·573 342	30	290	6·016 625	20
141	4·442 692	73	191	5·068 161	43	241	5·582 834	28	291	6·024 907	21
142	4·456 698	73	192	5·079 368	43	242	5·592 298	28	292	6·033 168	20
143	4·470 631	72	193	5·090 532	41	243	5·601 734	28	293	6·041 409	20
144	4·484 492	72	194	5·101 655	43	244	5·611 142	29	294	6·049 630	·21
145	4·498 281	69	195	5·112 735	41	245	5·620 521	26	295	6·057 830	19
146	4·512 001	70	196	5·123 774	42	246	5·629 874	29	296	6·066 011	21
147	4·525 651	69	197	5·134 771	40	247	5·639 198	27	297	6·074 171	19
148	4·539 232	67	198	5·145 728	40	248	5·648 495	27	298	6·082 312	19
149	4·552 746	67	199	5·156 645	41	249	5·657 765	26	299	6·090 434	20
150	4·566 193	66	200	5·167 521	39	250	5·667 009	28	300	6·098 536	20

TABLE 1.

D	μ	δ^2	D	μ	δ^2	D	μ	δ^2	D	μ	δ^2
300	6·098 536	20	350	6·481 031	16	400	6·826 234	12	450	7·141 974	10
301	6·106 618	19	351	6·488 269	14	401	6·832 816	12	451	7·148 029	10
302	6·114 681	19	352	6·495 493	15	402	6·839 386	11	452	7·154 074	9
303	6·122 725	19	353	6·502 702	15	403	6·845 945	12	453	7·160 110	9
304	6·130 750	19	354	6·509 896	14	404	6·852 492	11	454	7·166 137	10
305	6·138 756	18	355	6·517 076	14	405	6·859 028	12	455	7·172 154	9
306	6·146 744	20	356	6·524 242	15	406	6·865 552	11	456	7·178 162	9
307	6·154 712	18	357	6·531 393	14	407	6·872 065	11	457	7·184 161	10
308	6·162 662	19	358	6·538 530	15	408	6·878 567	12	458	7·190 150	9
309	6·170 593	18	359	6·545 652	13	409	6·885 057	11	459	7·196 130	9
310	6·178 506	18	360	6·552 761	15	410	6·891 536	11	460	7·202 101	10
311	6·186 401	19	361	6·559 855	13	411	6·898 004	12	461	7·208 062	8
312	6·194 277	17	362	6·566 936	15	412	6·904 460	10	462	7·214 015	10
313	6·202 136	19	363	6·574 002	13	413	6·910 906	12	463	7·219 958	9
314	6·209 976	18	364	6·581 055	14	414	6·917 340	11	464	7·225 892	8
315	6·217 798	17	365	6·588 094	14	415	6·923 763	10	465	7·231 818	10
316	6·225 603	18	366	6·595 119	14	416	6·930 176	12	466	7·237 734	9
317	6·233 390	18	367	6·602 130	13	417	6·936 577	10	467	7·243 641	8
318	6·241 159	17	368	6·609 128	14	418	6·942 968	12	468	7·249 540	10
319	6·248 911	17	369	6·616 112	13	419	6·949 347	10	469	7·255 429	8
320	6·256 646	18	370	6·623 083	14	420	6·955 716	10	470	7·261 310	10
321	6·264 363	17	371	6·630 040	13	421	6·962 075	12	471	7·267 181	8
322	6·272 063	17	372	6·636 984	13	422	6·968 422	10	472	7·273 044	9
323	6·279 746	18	373	6·643 915	14	423	6·974 759	11	473	7·278 898	8
324	6·287 411	16	374	6·650 832	13	424	6·981 085	11	474	7·284 744	10
325	6·295 060	17	375	6·657 736	13	425	6·987 400	10	475	7·290 580	8
326	6·302 692	17	376	6·664 627	13	426	6·993 705	10	476	7·296 408	8
327	6·310 307	16	377	6·671 505	12	427	7·000 000	11	477	7·302 228	9
328	6·317 906	17	378	6·678 371	14	428	7·006 284	10	478	7·308 039	9
329	6·325 488	17	379	6·685 223	13	429	7·012 558	11	479	7·313 841	9
330	6·333 053	15	380	6·692 062	13	430	7·018 821	10	480	7·319 634	8
331	6·340 603	18	381	6·698 888	12	431	7·025 074	10	481	7·325 419	8
332	6·348 135	15	382	6·705 702	13	432	7·031 317	11	482	7·331 196	9
333	6·355 652	17	383	6·712 503	12	433	7·037 549	9	483	7·336 964	8
334	6·363 152	15	384	6·719 292	13	434	7·043 772	11	484	7·342 724	9
335	6·370 637	17	385	6·726 068	13	435	7·049 984	10	485	7·348 475	8
336	6·378 105	15	386	6·732 831	12	436	7·056 186	10	486	7·354 218	8
337	6·385 558	17	387	6·739 582	13	437	7·062 378	10	487	7·359 953	9
338	6·392 994	15	388	6·746 320	12	438	7·068 560	11	488	7·365 679	8
339	6·400 415	16	389	6·753 046	12	439	7·074 731	9	489	7·371 397	8
340	6·407 820	15	390	6·759 760	12	440	7·080 893	10	490	7·377 107	9
341	6·415 210	16	391	6·766 462	13	441	7·087 045	9	491	7·382 808	7
342	6·422 584	15	392	6·773 151	12	442	7·093 188	11	492	7·388 502	9
343	6·429 943	15	393	6·779 828	12	443	7·099 320	10	493	7·394 187	8
344	6·437 287	16	394	6·786 493	11	444	7·105 442	9	494	7·399 864	8
345	6·444 615	15	395	6·793 147	13	445	7·111 555	10	495	7·405 533	8
346	6·451 928	15	396	6·799 788	12	446	7·117 658	9	496	7·411 194	9
347	6·459 226	15	397	6·806 417	12	447	7·123 752	11	497	7·416 846	7
348	6·466 509	15	398	6·813 034	11	448	7·129 835	9	498	7·422 491	8
349	6·473 777	14	399	6·819 640	12	449	7·135 909	9	499	7·428 128	8
350	6·481 031	16	400	6·826 234	12	450	7·141 974	10	500	7·433 757	8

HARLEY WOOD.

TABLE 1.

D	μ	δ²	D	μ	δ²	D	μ	δ²	D	μ	δ²
500	7·433 757	8	550	7·705 616	7	600	7·960 602	6	650	8·201 085	4
501	7·439 378	8	551	7·710 872	6	601	7·965 547	6	651	8·205 761	6
502	7·444 991	8	552	7·716 122	8	602	7·970 486	6	652	8·210 431	5
503	7·450 596	8	553	7·721 364	6	603	7·975 419	5	653	8·215 096	4
504	7·456 193	7	554	7·726 600	6	604	7·980 347	6	654	8·219 757	6
505	7·461 783	9	555	7·731 830	7	605	7·985 269	6	655	8·224 412	5
506	7·467 364	7	556	7·737 053	7	606	7·990 185	6	656	8·229 062	4
507	7·472 938	8	557	7·742 269	6	607	7·995 095	5	657	8·233 708	6
508	7·478 504	8	558	7·747 479	7	608	8·000 000	6	658	8·238 348	4
509	7·484 062	7	559	7·752 682	6	609	8·004 899	5	659	8·242 984	6
510	7·489 613	8	560	7·757 879	7	610	8·009 793	6	660	8·247 614	4
511	7·495 156	7	561	7·763 069	7	611	8·014 681	6	661	8·252 240	5
512	7·500 692	9	562	7·768 252	6	612	8·019 563	6	662	8·256 861	5
513	7·506 219	7	563	7·773 429	6	613	8·024 439	4	663	8·261 477•	5
514	7·511 739	7	564	7·778 600	7	614	8·029 311	7	664	8·266 088	5
515	7·517 252	8	565	7·783 764	6	615	8·034 176	5	665	8·270 694	5
516	7·522 757	7	566	7·788 922	6	616	8·039 036	5	666	8·275 295	4
517	7·528 255	8	567	7·794 074	7	617	8·043 891	6	667	8·279 892	5
518	7·533 745	8	568	7·799 219	7	618	8·048 740	6	668	8·284 484	6
519	7·539 227	7	569	7·804 357	6	619	8·053 583	5	669	8·289 070	3
520	7·544 702	7	570	7·809 489	6	620	8·058 421	5	670	8·293 653	6
521	7·550 170	8	571	7·814 615	6	621	8·063 254	6	671	8·298 230	5
522	7·555 630	7	572	7·819 735	6	622	8·068 081	6	672	8·302 802	4
523	7·561 083	7	573	7·824 849	7	623	8·072 902	5	673	8·307 370	5
524	7·566 529	8	574	7·829 956	6	624	8·077 718	5	674	8·311 933	4
525	7·571 967	7	575	7·835 057	7	625	8·082 529	5	675	8·316 492	6
526	7·577 398	7	576	7·840 151	5	626	8·087 335	6	676	8·321 045	4
527	7·582 822	7	577	7·845 240	7	627	8·092 135	6	677	8·325 594	5
528	7·588 239	8	578	7·850 322	6	628	8·096 929	4	678	8·330 138	4
529	7·593 648	7	579	7·855 398	6	629	8·101 719	6	679	8·334 678	5
530	7·599 050	7	580	7·860 468	6	630	8·106 503	6	680	8·339 213	5
531	7·604 445	7	581	7·865 532	7	631	8·111 281	4	681	8·343 743	4
532	7·609 833	8	582	7·870 589	5	632	8·116 055	6	682	8·348 269	6
533	7·615 213	6	583	7·875 641	7	633	8·120 823	5	683	8·352 789	3
534	7·620 587	8	584	7·880 686	5	634	8·125 586	6	684	8·357 306	6
535	7·625 953	6	585	7·885 726	7	635	8·130 343	4	685	8·361 817	4
536	7·631 313	8	586	7·890 759	5	636	8·135 096	6	686	8·366 324	4
537	7·636 665	7	587	7·895 787	7	637	8·139 843	5	687	8·370 827	5
538	7·642 010	6	588	7·900 808	6	638	8·144 585	6	688	8·375 325	5
539	7·647 349	8	589	7·905 823	5	639	8·149 321	4	689	8·379 818	4
540	7·652 680	6	590	7·910 833	7	640	8·154 053	6	690	8·384 307	5
541	7·658 005	8	591	7·915 836	5	641	8·158 779	5	691	8·388 791	4
542	7·663 322	6	592	7·920 834	7	642	8·163 500	5	692	8·393 271	5
543	7·668 633	7	593	7·925 825	5	643	8·168 216	5	693	8·397 746	4
544	7·673 937	8	594	7·930 811	6	644	8·172 927	5	694	8·402 217•	5
545	7·679 233	6	595	7·935 791	6	645	8·177 633	5	695	8·406 683	4
546	7·684 523	6	596	7·940 765	6	646	8·182 334	6	696	8·411 145	5
547	7·689 807	8	597	7·945 733	6	647	8·187 029	4	697	8·415 602	4
548	7·695 083	6	598	7·950 695	6	648	8·191 720	6	698	8·420 055	5
549	7·700 353	7	599	7·955 651	5	649	8·196 405	5	699	8·424 503	4
550	7·705 616	7	600	7·960 602	6	650	8·201 085	4	700	8·428 947	5

TABLE 1.

D	μ	D	μ	D	μ	D	μ
700	$8\cdot428\ 947_{4439}$	750	$8\cdot645\ 707_{4231}$	800	$8\cdot852\ 614_{4046}$	850	$9\cdot050\ 708_{3878}$
701	$8\cdot433\ 386_{4435}$	751	$8\cdot649\ 938_{4227}$	801	$8\cdot856\ 660_{4041}$	851	$9\cdot054\ 586_{3875}$
702	$8\cdot437\ 821_{4431}$	752	$8\cdot654\ 165_{4223}$	802	$8\cdot860\ 701_{4038}$	852	$9\cdot058\ 461_{3872}$
703	$8\cdot442\ 252_{4426}$	753	$8\cdot658\ 388_{4219}$	803	$8\cdot864\ 739_{4035}$	853	$9\cdot062\ 333_{3868}$
704	$8\cdot446\ 678_{4422}$	754	$8\cdot662\ 607_{4216}$	804	$8\cdot868\ 774_{4031}$	854	$9\cdot066\ 201_{3866}$
705	$8\cdot451\ 100_{4418}$	755	$8\cdot666\ 823_{4211}$	805	$8\cdot872\ 805_{4027}$	855	$9\cdot070\ 067_{3863}$
706	$8\cdot455\ 518_{4413}$	756	$8\cdot671\ 034_{4208}$	806	$8\cdot876\ 832_{4025}$	856	$9\cdot073\ 930_{3859}$
707	$8\cdot459\ 931_{4408}$	757	$8\cdot675\ 242_{4203}$	807	$8\cdot880\ 857_{4020}$	857	$9\cdot077\ 789_{3856}$
708	$8\cdot464\ 339_{4405}$	758	$8\cdot679\ 445_{4200}$	808	$8\cdot884\ 877_{4017}$	858	$9\cdot081\ 645_{3853}$
709	$8\cdot468\ 744_{4400}$	759	$8\cdot683\ 645_{4196}$	809	$8\cdot888\ 894_{4014}$	859	$9\cdot085\ 498_{3850}$
710	$8\cdot473\ 144_{4395}$	760	$8\cdot687\ 841_{4192}$	810	$8\cdot892\ 908_{4010}$	860	$9\cdot089\ 348_{3847}$
711	$8\cdot477\ 539_{4392}$	761	$8\cdot692\ 033_{4188}$	811	$8\cdot896\ 918_{4007}$	861	$9\cdot093\ 195_{3844}$
712	$8\cdot481\ 931_{4387}$	762	$8\cdot696\ 221_{4185}$	812	$8\cdot900\ 925_{4004}$	862	$9\cdot097\ 039_{3840}$
713	$8\cdot486\ 318_{4383}$	763	$8\cdot700\ 406_{4180}$	813	$8\cdot904\ 929_{4000}$	863	$9\cdot100\ 879_{3838}$
714	$8\cdot490\ 701_{4378}$	764	$8\cdot704\ 586_{4177}$	814	$8\cdot908\ 929_{3996}$	864	$9\cdot104\ 717_{3834}$
715	$8\cdot495\ 079_{4375}$	765	$8\cdot708\ 763_{4173}$	815	$8\cdot912\ 925_{3993}$	865	$9\cdot108\ 551_{3832}$
716	$8\cdot499\ 454_{4370}$	766	$8\cdot712\ 936_{4169}$	816	$8\cdot916\ 918_{3990}$	866	$9\cdot112\ 383_{3828}$
717	$8\cdot503\ 824_{4365}$	767	$8\cdot717\ 105_{4166}$	817	$8\cdot920\ 908_{3987}$	867	$9\cdot116\ 211_{3825}$
718	$8\cdot508\ 189_{4362}$	768	$8\cdot721\ 271_{4161}$	818	$8\cdot924\ 895_{3983}$	868	$9\cdot120\ 036_{3822}$
719	$8\cdot512\ 551_{4357}$	769	$8\cdot725\ 432_{4158}$	819	$8\cdot928\ 878_{3979}$	869	$9\cdot123\ 858_{3820}$
720	$8\cdot516\ 908_{4353}$	770	$8\cdot729\ 590_{4154}$	820	$8\cdot932\ 857_{3976}$	870	$9\cdot127\ 678_{3816}$
721	$8\cdot521\ 261_{4349}$	771	$8\cdot733\ 744_{4151}$	821	$8\cdot936\ 833_{3973}$	871	$9\cdot131\ 494_{3813}$
722	$8\cdot525\ 610_{4344}$	772	$8\cdot737\ 895_{4146}$	822	$8\cdot940\ 806_{3970}$	872	$9\cdot135\ 307_{3810}$
723	$8\cdot529\ 954_{4341}$	773	$8\cdot742\ 041_{4143}$	823	$8\cdot944\ 776_{3966}$	873	$9\cdot139\ 117_{3807}$
724	$8\cdot534\ 295_{4336}$	774	$8\cdot746\ 184_{4139}$	824	$8\cdot948\ 742_{3963}$	874	$9\cdot142\ 924_{3804}$
725	$8\cdot538\ 631_{4332}$	775	$8\cdot750\ 323_{4136}$	825	$8\cdot952\ 705_{3959}$	875	$9\cdot146\ 728_{3801}$
726	$8\cdot542\ 963_{4328}$	776	$8\cdot754\ 459_{4131}$	826	$8\cdot956\ 664_{3956}$	876	$9\cdot150\ 529_{3798}$
727	$8\cdot547\ 291_{4324}$	777	$8\cdot758\ 590_{4128}$	827	$8\cdot960\ 620_{3953}$	877	$9\cdot154\ 327_{3795}$
728	$8\cdot551\ 615_{4320}$	778	$8\cdot762\ 718_{4125}$	828	$8\cdot964\ 573_{3950}$	878	$9\cdot158\ 122_{3791}$
729	$8\cdot555\ 935_{4315}$	779	$8\cdot766\ 843_{4120}$	829	$8\cdot968\ 523_{3946}$	879	$9\cdot161\ 913_{3789}$
730	$8\cdot560\ 250_{4312}$	780	$8\cdot770\ 963_{4117}$	830	$8\cdot972\ 469_{3943}$	880	$9\cdot165\ 702_{3786}$
731	$8\cdot564\ 562_{4307}$	781	$8\cdot775\ 080_{4114}$	831	$8\cdot976\ 412_{3939}$	881	$9\cdot169\ 488_{3783}$
732	$8\cdot568\ 869_{4303}$	782	$8\cdot779\ 194_{4109}$	832	$8\cdot980\ 351_{3937}$	882	$9\cdot173\ 271_{3780}$
733	$8\cdot573\ 172_{4299}$	783	$8\cdot783\ 303_{4106}$	833	$8\cdot984\ 288_{3933}$	883	$9\cdot177\ 051_{3777}$
734	$8\cdot577\ 471_{4295}$	784	$8\cdot787\ 409_{4103}$	834	$8\cdot988\ 221_{3929}$	884	$9\cdot180\ 828_{3774}$
735	$8\cdot581\ 766_{4291}$	785	$8\cdot791\ 512_{4098}$	835	$8\cdot992\ 150_{3927}$	885	$9\cdot184\ 602_{3771}$
736	$8\cdot586\ 057_{4287}$	786	$8\cdot795\ 610_{4095}$	836	$8\cdot996\ 077_{3923}$	886	$9\cdot188\ 373_{3769}$
737	$8\cdot590\ 344_{4283}$	787	$8\cdot799\ 705_{4092}$	837	$9\cdot000\ 000_{3920}$	887	$9\cdot192\ 142_{3765}$
738	$8\cdot594\ 627_{4278}$	788	$8\cdot803\ 797_{4088}$	838	$9\cdot003\ 920_{3917}$	888	$9\cdot195\ 907_{3762}$
739	$8\cdot598\ 905_{4275}$	789	$8\cdot807\ 885_{4084}$	839	$9\cdot007\ 837_{3913}$	889	$9\cdot199\ 669_{3759}$
740	$8\cdot603\ 180_{4271}$	790	$8\cdot811\ 969_{4080}$	840	$9\cdot011\ 750_{3910}$	890	$9\cdot203\ 428_{3757}$
741	$8\cdot607\ 451_{4266}$	791	$8\cdot816\ 049_{4077}$	841	$9\cdot015\ 660_{3907}$	891	$9\cdot207\ 185_{3753}$
742	$8\cdot611\ 717_{4263}$	792	$8\cdot820\ 126_{4074}$	842	$9\cdot019\ 567_{3904}$	892	$9\cdot210\ 938_{3751}$
743	$8\cdot615\ 980_{4259}$	793	$8\cdot824\ 200_{4070}$	843	$9\cdot023\ 471_{3901}$	893	$9\cdot214\ 689_{3747}$
744	$8\cdot620\ 239_{4254}$	794	$8\cdot828\ 270_{4066}$	844	$9\cdot027\ 372_{3897}$	894	$9\cdot218\ 436_{3745}$
745	$8\cdot624\ 493_{4251}$	795	$8\cdot832\ 336_{4063}$	845	$9\cdot031\ 269_{3894}$	895	$9\cdot222\ 181_{3742}$
746	$8\cdot628\ 744_{4247}$	796	$8\cdot836\ 399_{4059}$	846	$9\cdot035\ 163_{3891}$	896	$9\cdot225\ 923_{3739}$
747	$8\cdot632\ 991_{4243}$	797	$8\cdot840\ 458_{4056}$	847	$9\cdot039\ 054_{3888}$	897	$9\cdot229\ 662_{3736}$
748	$8\cdot637\ 234_{4238}$	798	$8\cdot844\ 514_{4052}$	848	$9\cdot042\ 942_{3884}$	898	$9\cdot233\ 398_{3733}$
749	$8\cdot641\ 472_{4235}$	799	$8\cdot848\ 566_{4048}$	849	$9\cdot046\ 826_{3882}$	899	$9\cdot237\ 131_{3730}$
750	$8\cdot645\ 707$	800	$8\cdot852\ 614$	850	$9\cdot050\ 708$.	900	$9\cdot240\ 861$

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TABLE 1.   TABLE 2.

D	μ	D	μ
900	$9 \cdot 240\ 861_{3728}$	950	$9 \cdot 423\ 820_{3590}$
901	$9 \cdot 244\ 589_{3724}$	951	$9 \cdot 427\ 410_{3588}$
902	$9 \cdot 248\ 313_{3722}$	952	$9 \cdot 430\ 998_{3585}$
903	$9 \cdot 252\ 035_{3719}$	953	$9 \cdot 434\ 583_{3582}$
904	$9 \cdot 255\ 754_{3716}$	954	$9 \cdot 438\ 165_{3580}$
905	$9 \cdot 259\ 470_{3713}$	955	$9 \cdot 441\ 745_{3578}$
906	$9 \cdot 263\ 183_{3710}$	956	$9 \cdot 445\ 323_{3574}$
907	$9 \cdot 266\ 893_{3707}$	957	$9 \cdot 448\ 897_{3572}$
908	$9 \cdot 270\ 600_{3705}$	958	$9 \cdot 452\ 469_{3570}$
909	$9 \cdot 274\ 305_{3702}$	959	$9 \cdot 456\ 039_{3567}$
910	$9 \cdot 278\ 007_{3699}$	960	$9 \cdot 459\ 606_{3564}$
911	$9 \cdot 281\ 706_{3696}$	961	$9 \cdot 463\ 170_{3562}$
912	$9 \cdot 285\ 402_{3693}$	962	$9 \cdot 466\ 732_{3559}$
913	$9 \cdot 289\ 095_{3691}$	963	$9 \cdot 470\ 291_{3557}$
914	$9 \cdot 292\ 786_{3687}$	964	$9 \cdot 473\ 848_{3554}$
915	$9 \cdot 296\ 473_{3685}$	965	$9 \cdot 477\ 402_{3552}$
916	$9 \cdot 300\ 158_{3683}$	966	$9 \cdot 480\ 954_{3549}$
917	$9 \cdot 303\ 841_{3679}$	967	$9 \cdot 484\ 503_{3546}$
918	$9 \cdot 307\ 520_{3676}$	968	$9 \cdot 488\ 049_{3544}$
919	$9 \cdot 311\ 196_{3674}$	969	$9 \cdot 491\ 593_{3542}$
920	$9 \cdot 314\ 870_{3671}$	970	$9 \cdot 495\ 135_{3539}$
921	$9 \cdot 318\ 541_{3669}$	971	$9 \cdot 498\ 674_{3536}$
922	$9 \cdot 322\ 210_{3665}$	972	$9 \cdot 502\ 210_{3534}$
923	$9 \cdot 325\ 875_{3663}$	973	$9 \cdot 505\ 744_{3531}$
924	$9 \cdot 329\ 538_{3660}$	974	$9 \cdot 509\ 275_{3529}$
925	$9 \cdot 333\ 198_{3657}$	975	$9 \cdot 512\ 804_{3526}$
926	$9 \cdot 336\ 855_{3655}$	976	$9 \cdot 516\ 330_{3524}$
927	$9 \cdot 340\ 510_{3651}$	977	$9 \cdot 519\ 854_{3521}$
928	$9 \cdot 344\ 161_{3649}$	978	$9 \cdot 523\ 375_{3519}$
929	$9 \cdot 347\ 810_{3647}$	979	$9 \cdot 526\ 894_{3517}$
930	$9 \cdot 351\ 457_{3643}$	980	$9 \cdot 530\ 411_{3514}$
931	$9 \cdot 355\ 100_{3641}$	981	$9 \cdot 533\ 925_{3511}$
932	$9 \cdot 358\ 741_{3639}$	982	$9 \cdot 537\ 436_{3509}$
933	$9 \cdot 362\ 380_{3635}$	983	$9 \cdot 540\ 945_{3506}$
934	$9 \cdot 366\ 015_{3633}$	984	$9 \cdot 544\ 451_{3504}$
935	$9 \cdot 369\ 648_{3630}$	985	$9 \cdot 547\ 955_{3502}$
936	$9 \cdot 373\ 278_{3627}$	986	$9 \cdot 551\ 457_{3499}$
937	$9 \cdot 376\ 905_{3625}$	987	$9 \cdot 554\ 956_{3496}$
938	$9 \cdot 380\ 530_{3622}$	988	$9 \cdot 558\ 452_{3495}$
939	$9 \cdot 384\ 152_{3620}$	989	$9 \cdot 561\ 947_{3491}$
940	$9 \cdot 387\ 772_{3616}$	990	$9 \cdot 565\ 438_{3490}$
941	$9 \cdot 391\ 388_{3615}$	991	$9 \cdot 568\ 928_{3486}$
942	$9 \cdot 395\ 003_{3611}$	992	$9 \cdot 572\ 414_{3485}$
943	$9 \cdot 398\ 614_{3609}$	993	$9 \cdot 575\ 899_{3482}$
944	$9 \cdot 402\ 223_{3606}$	994	$9 \cdot 579\ 381_{3479}$
945	$9 \cdot 405\ 829_{3603}$	995	$9 \cdot 582\ 860_{3477}$
946	$9 \cdot 409\ 432_{3601}$	996	$9 \cdot 586\ 337_{3475}$
947	$9 \cdot 413\ 033_{3598}$	997	$9 \cdot 589\ 812_{3472}$
948	$9 \cdot 416\ 631_{3596}$	998	$9 \cdot 593\ 284_{3470}$
949	$9 \cdot 420\ 227_{3593}$	999	$9 \cdot 596\ 754_{3468}$
950	$9 \cdot 423\ 820$	1000	$9 \cdot 600\ 222$

$4/D^{1/3}$	R
0·00	$0 \cdot 000\ 000_{0}$
·01	000_{0}
·02	000_{0}
·03	000_{0}
·04	000_{0}
0·05	$0 \cdot 000\ 000_{0}$
·06	000_{0}
·07	000_{0}
·08	000_{0}
·09	000_{0}
0·10	$0 \cdot 000\ 000_{0}$
·11	000_{1}
·12	001_{0}
·13	001_{0}
·14	001_{1}
0·15	$0 \cdot 000\ 002_{0}$
·16	002_{1}
·17	003_{1}
·18	004_{1}
·19	005_{2}
0·20	$0 \cdot 000\ 007_{2}$
·21	009_{2}
·22	011_{3}
·23	014_{3}
·24	017_{4}
0·25	$0 \cdot 000\ 021_{4}$
·26	025_{5}
·27	030_{7}
·28	037_{7}
·29	044_{8}
0·30	$0 \cdot 000\ 052_{9}$
·31	061_{11}
·32	072_{12}
·33	084_{13}
·34	097_{16}
0·35	$0 \cdot 000\ 113_{17}$
·36	130_{19}
·37	149_{22}
·38	171_{24}
·39	195_{27}
0·40	$0 \cdot 000\ 222_{29}$
·41	251

When D>1000 use
$\mu = D^{1/3} - 4/D^{1/3} + R$

as it is the one convenient in the other method suggested it was thought desirable to maintain uniformity.

Next is provided in Table 2 a convenient way of dealing with the problem when $D > 1,000$. Tartaglia's solution of the cubic equation gives

$$\mu = \left\{ \frac{D}{2} + \frac{D}{2}\left(1 + \frac{256}{D^2}\right)^{1/2} \right\}^{1/3} + \left\{ \frac{D}{2} - \frac{D}{2}\left(1 + \frac{256}{D^2}\right)^{1/2} \right\}^{1/3}$$

$$= D^{1/3}\left\{ \frac{1}{2} + \frac{1}{2}\left(1 + \frac{256}{D^2}\right)^{1/2} \right\}^{1/3} + D^{1/3}\left\{ \frac{1}{2} - \frac{1}{2}\left(1 + \frac{256}{D^2}\right)^{1/2} \right\}^{1/3}$$

$$= D^{1/3} - \frac{4}{D^{1/3}} + \frac{2^6}{3} \frac{1}{D^{5/3}} + \frac{2^8}{3} \frac{1}{D^{7/3}} - \frac{2^{14}}{9} \frac{1}{D^{11/3}} - \frac{7 \cdot 2^{14}}{9} \frac{1}{D^{13/3}} + \cdots,$$

where the necessary binomial expansions are easily justified. Now place $4/D^{1/3} = d$ and write the solution

$$\mu = D^{1/3} - \frac{4}{D^{1/3}} + R,$$

where $$R = \frac{1}{2^4 \cdot 3}d^5 + \frac{1}{2^6 \cdot 3}d^7 - \frac{1}{2^8 \cdot 3^2}d^{11} - \frac{7}{2^{12} \cdot 3^2}d^{13} + \cdots$$

Table 2 gives R with argument $4/D^{1/3}$ and the solution is performed for $D > 1000$ by obtaining $D^{1/3}$ by linear interpolation in Barlow's tables (Comrie, 1941), then calculating $4/D^{1/3}$ and finding R from the table. When $D > 12,500$, taking the computer beyond the table of cube roots in Barlow, one of the methods of finding cube roots explained in the introduction to that invaluable work may be used. The table was calculated from the series for R and the same remarks apply as for Table I except that no subtabulation was done, every value being computed.

For the computation of the other coordinate, λ, in the plane of the orbit μ^2 is needed. No table of μ^2 is given since it is quicker to calculate the square of a seven figure number with a machine than to interpolate for it from a table with argument D.

The constants of the equator are computed for the orbit from the formulae

$$A_x = q\{\cos \omega \cos \Omega - \sin \omega \sin \Omega \cos i\},$$
$$B_x = q\{-\sin \omega \cos \Omega - \cos \omega \sin \Omega \cos i\},$$
$$A_y = q\{(\sin \omega \cos \Omega \cos i + \cos \omega \sin \Omega) \cos \varepsilon - \sin \omega \sin i \sin \varepsilon\},$$
$$B_y = q\{(\cos \omega \cos \Omega \cos i - \sin \omega \sin \Omega) \cos \varepsilon - \cos \omega \sin i \sin \varepsilon\},$$
$$A_z = q\{\sin \omega \sin i \cos \varepsilon + (\sin \omega \cos \Omega \cos i + \cos \omega \sin \Omega) \sin \varepsilon\},$$
$$B_z = q\{\cos \omega \sin i \cos \varepsilon + (\cos \omega \cos \Omega \cos i - \sin \omega \sin \Omega) \sin \varepsilon\},$$

with the check formula

$$A_x B_x + A_y B_y + A_z B_z = 0.$$

Then having obtained μ in one of the above ways the rectangular equatorial heliocentric coordinates (x, y, z) may be calculated from

$$x = A_x - \frac{A_x}{4}\mu^2 + B_x\mu,$$

$$y = A_y - \frac{A_y}{4}\mu^2 + B_y\mu,$$

$$z = A_z - \frac{A_z}{4}\mu^2 + B_z\mu.$$

REFERENCES.

Chambers, G. F., 1889. Handbook of Descriptive and Practical Astronomy. Clarendon
     Press, Oxford.
————————— 1909. The Story of the Comets. Clarendon Press, Oxford.
Comrie, L. J., 1941. Barlow's Tables of Squares, Cubes, Square Roots, Cube Roots and Re-
     ciprocals. Spon, London.
Crommelin, A. C. D., 1925. Comet Catalogue. *Mem, Brit. astr. Ass.*, **26**, Part 2.
————————— 1932. Continuation of the Comet Catalogue. *Mem. Brit. astr. Ass.*,
     30, Part 1.
Galle, J. G., 1894. Verzeichniss der Elemente der bisher berechneten Cometbahnen. Wilhelm
     Engelmann, Leipzig.
Oppolzer, T. d', 1886. Traité de la Détermination des Orbites des Comètes et des Planètes.
     Gauthier-Villars, Paris.
Strömgren, B., 1927. Tables giving tan v/2 and tan² v/2 in Parabolic Motion. *Mem. Brit.
     astr. Ass.*, **27**, Part 2.
Subbotin, M. T., 1929. Formules et Tables pour le Calcul des Orbites et des Éphémérides.
     Publ. Obs. astr. Tashkent, 2.
Winlock, W. C., 1896. Tables of the Elements of Comet Orbits. *Publ. astr. Soc. Pacif.*, **8**, 141.
Wood, H., 1950. This Journal, **83**, 150. Also *Sydney Obs. Papers*, No. 10.

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RANK VARIATION IN VITRAIN AND RELATIONS TO THE PHYSICAL NATURE OF ITS CARBONISED PRODUCTS.

By NORA HINDER, B.Sc.

INTRODUCTION.

The investigations recorded in this paper were carried out with the object of studying variations in the chemical properties of vitrains of all ranks, and also for the purpose of obtaining some fundamental data regarding general relationships between rank of vitrain and the physical nature of products of carbonisation under low-temperature conditions. Vitrain, the purest and most homogeneous of the petrological constituents in coal, was used to obtain comparable results and to avoid the influence of varying proportions of banded constituents which may obscure the significance of results obtained from seam-samples.

The present work on relation between rank of vitrain and physical nature of carbonisation products must be regarded as a preliminary reconnaissance in a wide field of problems where very little fundamental data is available. Carbonisation was carried out under one specific set of conditions, and results represent relationships for those conditions. The nature of cokes and chars depends on many factors such as temperature, rate of heating, pressure on the carbonising mass, and coarseness of the materials before heating. Variation in any of these factors may produce somewhat different results, and a great deal of research is required to elucidate all aspects of the problem. However, it is believed that results, recorded in this paper, have established some general relationships between degree of development of micelle structure in vitrain and the ultra-fine structure of its carbonisation products.

SELECTION AND PREPARATION OF MATERIAL.

Coals were selected to include as many members of the metamorphic series as possible, from immature peat to anthracite and graphite. The materials range in geological age from Carboniferous to Pleistocene. All important Australian coalfields are represented and materials are included from Great Britain, Germany, Canada, the United States and Antarctica. In the case of coals of sub-bituminous rank or lower, pieces of woody material were selected as the precursors of vitrain, and at the extreme low-rank end of the series a contemporary wood, *Eucalyptus corymbosa*, was included for comparative purposes. Where the coal was of higher rank, specimens containing well-developed vitrain bands were selected, and two or more individual bands, from 0·2 to 0·5 inch in thickness, were separated by hand from each specimen, or from several specimens from the same locality. In the graphitic coal from Rhode Island, U.S.A., the different petrological constituents could not be recognised, and although the coal was used to mark the high-rank extreme of the series, it must be regarded as a *whole coal* sample and not a true vitrain. Fifty-three different coals were selected to provide a complete range in rank. From these, vitrain was carefully separated by hand and granular samples were prepared by crushing, with the minimum production of fines, to pass

through a sieve with circular perforations of 0·06 inch diameter and to be retained on a sieve with perforations of 0·04 inch diameter. Vitrains of sub-bituminous rank or lower (i.e. 79% carbon or less) which undergo permanent moisture changes on drying, were maintained in their original water-saturated condition in all cases where maximum inherent moisture was to be determined. Sieved and graded vitrain from coals of sub-bituminous rank or higher were water-saturated then washed with dilute hydrochloric acid (5% solution) to remove adherent mineral matter, particularly carbonates, deposited in cleat planes. All traces of acid were then washed out, and after setting aside a few grammes of the water-saturated material for determination of maximum inherent moisture, the rest of the sample was air-dried.

METHODS OF ANALYSIS AND EXPERIMENTAL TECHNIQUE.

Ultimate and proximate analyses of all samples were carried out by standard technique, using apparatus with slight modifications but generally similar to that described by Himus (1946). Results of analyses are listed in Table 1. Carbon, hydrogen, volatiles and fixed carbon values are quoted on the ash-free, dry basis. Maximum inherent moistures of vitrains and their carbonised products were determined by controlled vaporisation of adherent moisture (Dulhunty, 1947) and results are quoted as percentages, representing grammes of moisture per 100 grammes of dry material. Throughout this paper, all moisture values and references to moisture represent *maximum inherent moisture* which is the total amount of moisture held in the material when all openings, small enough to lower the vapour pressure of water, are filled, and no adherent moisture of normal vapour pressure is present. As described earlier, vitrains separated from coals of sub-bituminous rank or lower were prepared and maintained in their original water-saturated condition to avoid irreversible changes which occur on air drying (Dulhunty, 1948); therefore, maximum inherent moisture values represent a true index of the physical rank of the materials.

A test was designed with the object of studying bulk-volume changes in granular samples of vitrain as a result of carbonisation under free-swelling, low-temperature conditions of heating.

Carbonisation was carried out in an iron tube with an inside diameter of 0·5 inch, and an overall length of 3·2 inches, closed at each end by ground iron plugs. One plug, at the top of the tube, was provided with a central hole of 0·125 inch diameter, for escape of volatiles. A 3·5 inches length of $\frac{7}{16}$ iron rod was used as a plunger, to measure the depths of vitrain filled into the tube and the residue after carbonisation. The tube, with the lower plug in position, was held vertically and granular vitrain added to a depth of approximately 1·02 inches, measured by inserting the plunger and resting it on the surface of the material which had previously been thoroughly settled down to constant level by gentle tapping. The tube was then heated with the plunger in position, at 110° C. for two hours in an atmosphere of nitrogen, to dry the vitrain. After heating, the plunger was removed and the tube, closed with a cork, was cooled in a stoppered test tube, and the depth of dry vitrain, approximately one inch in all cases, was measured. The plunger was then withdrawn, the upper iron plug inserted, the tube placed in a vertical tube-furnace and heated from room temperature to 600° C. under time-temperature conditions similar to those employed in the Gray King assay. The tube was then removed from the furnace and allowed to cool, after which the iron plug was removed and the depth of carbonised residue measured by inserting the plunger. The difference between measurements before and after carbonisation, representing expansion or contraction, was expressed as a percentage of the depth of dry vitrain originally contained in the tube. Low-temperature carbonisation of all members of the

TABLE I.

Properties of Hand Separated Vitrains.

Spec. No.	Locality.	Geological Age.	Rank.	Percentage Ash.	At 925° C.		At 600° C.		Percentage Carbon.	Percentage Hydrogen.	Percentage Volume Change on Carbonising.
					Percentage Vols.	Percentage F.C.	Percentage Vols.	Percentage F.C.			
572	Rhode Island, U.S.A.	Carb.	Graphite.	14·1	3·8	96·2	—	—	97·3	2·0	0·0
622	South Wales, Great Britain	Carb.	Anthrac.	1·3	5·3	94·7	—	—	93·9	3·6	−2·0
567	Pennsylvania, U.S.A.	Carb.	Anthrac.	4·0	5·7	94·3	—	—	93·0	3·7	−1·1
497	Largenbrahm, Ruhr, Germany.	Carb.	Anthrac.	0·4	7·0	93·0	—	—	92·7	3·8	−3·3
525	Palmaise, Scotland	Carb.	Anthrac.	1·9	6·1	93·9	—	—	92·3	3·5	−4·5
208	Baralaba, Queensland	Perm.	Semi-Anthrac.	1·9	10·7	89·3	6·5	93·5	91·6	4·4	−13·1
28	Mittagong, N.S.W.	Perm.	Semi-Anthrac.	5·7	7·4	92·6	3·5	96·5	91·5	3·3	−11·1
161	York Plains, Tasmania	Trias.	Semi-Anthrac.	3·6	11·7	88·3	7·2	92·8	90·3	3·9	−2·9
36	Currabubula, N.S.W.	Perm.	High - rank Bitumin.	22·0	15·7	84·3	—	—	89·2	4·2	−7·1
310	Aberdare, N.S.W.	Perm.	High - rank Bitumin.	1·5	39·6	60·4	30·6	69·4	89·2	5·5	+136·0
314	Austinmer, N.S.W.	Perm.	High - rank Bitumin.	1·0	27·9	72·1	—	—	88·9	5·2	+598·0
313	Clifton, N.S.W.	Perm.	High - rank Bitumin.	0·9	25·5	74·5	16·3	83·7	88·8	4·1	+423·0
30	Balmain, N.S.W.	Perm.	High - rank Bitumin.	1·0	23·5	76·5	14·9	85·1	88·3	5·1	+89·0
443	Dapto, N.S.W.	Perm.	High - rank Bitumin.	2·5	29·0	71·0	—	—	88·1	5·3	+496·0
312	Helensburgh, N.S.W.	Perm.	High - rank Bitumin.	0·8	24·9	75·1	17·8	82·2	88·0	4·7	+476·7
644	Undercliffe, N.S.W.	Trias.	High - rank Bitumin.	0·7	36·1	63·9	—	—	85·3	4·9	+524·0
347 348	Borrima, N.S.W.	Perm.	High - rank Bitumin.	3·5	33·3	66·7	—	—	84·8	5·4	+99·1
646	Sydney, N.S.W.	Trias.	High - rank Bitumin.	0·8	36·3	63·7	—	—	84·2	5·1	+298·9
460	Catherine Hill Bay, N.S.W.	Perm.	High - rank Bitumin.	1·3	33·3	66·7	—	—	84·1	5·3	+60·5

(At 925° C. and At 600° C. columns are Ash-free, Dry Basis.)

TABLE I.—*Continued.*

Properties of Hand Separated Vitrains.—*Continued.*

Spec. No.	Locality.	Geological Age.	Rank.	Percentage Ash.	Ash-free, Dry Basis.						
					At 925° C.		At 600° C.		Percentage Carbon.	Percentage Hydrogen.	Percentage Volume Change on Carbonising.
					Percentage Vols.	Percentage F.C.	Percentage Vols.	Percentage F.C.			
458	Redhead, N.S.W.	Perm.	Med.-rank Bitumin.	2·6	36·9	63·1	—	—	83·7	5·7	+81·0
459	Belmont, N.S.W.	Perm.	Med.-rank Bitumin.	1·8	37·6	62·4	—	—	83·4	5·4	+21·0
288	Wonthaggi, Victoria	Jur.	Med.-rank Bitumin.	1·2	34·4	65·6	24·9	75·1	82·0	5·2	0·0
124	Mt. Nicholas, Tasmania	Trias.	Med.-rank Bitumin.	0·4	34·6	65·4	18·1	81·9	81·9	5·1	—4·0
169	Wallsend, N.S.W.	Perm.	Med.-rank Bitumin.	2·1	34·4	65·6	26·4	73·6	81·3	5·0	+2·0
174	Liddell, N.S.W.	Perm.	Med.-rank Bitumin.	3·0	40·9	59·1	31·5	68·5	81·0	6·8	+58·8
172	Rix Creek, N.S.W.	Perm.	Med.-rank Bitumin.	0·4	38·9	61·1	25·9	74·1	80·9	5·1	+49·0
181	Kandos, N.S.W.	Perm.	Med.-rank Bitumin.	0·6	36·3	63·7	27·6	72·4	80·8	5·1	+46·0
212	Mt. Mulligan, Queensland	Perm.	Med.-rank Bitumin.	1·6	29·7	70·3	19·9	80·1	80·7	4·8	—11·9
138	Wonthaggi, Victoria	Jur.	Med.-rank Bitumin.	1·0	38·2	61·8	27·8	72·2	80·3	4·9	+2·1
186	Seymour, Tasmania	Trias.	Low-rank Bitumin.	2·7	36·5	63·5	27·0	73·0	80·0	5·0	—12·8
461	Swansea, N.S.W.	Perm.	Low-rank Bitumin.	6·5	36·3	63·7	—	—	79·8	5·2	+7·6
143	Ipswich, Queensland.	Trias.	Low-rank Bitumin.	5·0	35·5	64·5	26·1	73·9	79·1	5·2	+2·8
209	Callide, Queensland	Jur.	Sub-Bitumin.	1·8	36·8	63·2	26·6	73·4	77·9	4·8	—24·7
317	Collie, Western Australia	Perm.	Sub-Bitumin.	2·4	32·9	67·1	—	—	76·6	5·9	—
120	Collie, Western Australia	Perm.	Sub-Bitumin.	1·9	34·7	65·3	29·7	70·3	74·8	4·9	—24·5
304	Leigh Creek, South Australia	Trias.	High-rank Brown Coal.	3·8	36·2	65·8	30·6	69·4	74·5	4·5	—22·4

TABLE I.—*Continued.*

Properties of Hand Separated Vitrains.—Continued.

Spec. No.	Locality.	Geological Age.	Rank.	Percentage Ash.	Ash-free, Dry Basis.						
					At 925° C.		At 600° C.		Percentage Carbon.	Percentage Hydrogen.	Percentage Volume Change on Carbonising.
					Percentage Vols.	Percentage F.C.	Percentage Vols.	Percentage F.C.			
296	Benwerrin, Victoria	Tert.	High - rank Brown Coal	2·5	36·5	63·5	30·3	69·7	72·9	4·4	−25·0
290-291	Leigh Creek, South Australia	Trias.	High - rank Brown Coal	6·5	41·9	58·1	34·5	65·5	71·9	4·5	−23·2
456	Moosonee, Canada	Cret.	Med. - rank Brown Coal	2·7	51·6	48·4	—	—	69·8	5·4	−42·2
457	Bovey Tracey, England	Tert.	Med - rank. Brown Coal	1·9	54·4	45·6	—	—	69·6	5·6	−40·5
88	Berridale, N.S.W.	Tert.	Med. - rank Brown Coal	3·2	53·8	46·2	38·4	61·6	68·9	5·5	−28·5
299	Yallourn, Victoria	Tert.	Med. - rank Brown Coal	1·1	52·4	47·6	43·0	57·0	68·4	5·4	−23·7
454	Liblar, Germany	Tert.	Med. - rank Brown Coal	1·4	54·7	45·3	—	—	68·3	5·5	−51·6
286	Bacchus Marsh, Victoria	Tert.	Med. - rank Brown Coal	4·5	50·3	49·7	42·7	57·3	68·0	5·1	−25·9
136	Yallourn, Victoria	Tert.	Med. - rank Brown Coal	1·8	60·1	39·9	41·8	58·2	67·4	4·3	−24·5
142	Kiandra, N.S.W.	Tert.	Low - rank Brown Coal	0·6	62·0	38·0	51·7	48·3	66·3	6·1	−28·7
298	Kerguelen Island, Ant. arctica.	Tert.	Low - rank Brown Coal	7·1	52·5	47·5	44·2	55·8	63·8	5·1	−23·0
283	Kelso, Tasmania	Mioc.	Low - rank Brown Coal	0·5	55·3	44·7	45·3	54·7	63·4	5·1	−33·7
455	Cologne, Germany	Tert.	Low - rank Brown Coal	1·8	64·6	35·4	—	—	62·5	5·9	−50·1
104	Kiandra, N.S.W.	Tert.	Low - rank Brown Coal	0·4	76·4	23·6	62·8	37·2	59·2	6·1	−21·6
453	Haltern, Germany	Tert.	Peat.	0·3	87·7	12·3	—	—	58·4	7·3	−66·0
282	*Euc. corymbosa*, Victoria	Contemp.		0·1	82·1	17·9	72·6	27·4	52·1	5·6	−38·8
75	Potts Point, N.S.W.	Pleist.	Peat.	5·1	75·0	25·0	69·7	30·3	51·3	5·7	−31·6

series was carried out, and results (see Table 1) recorded as positive values where expansion took place, and negative values where contraction occurred.

Results with a high degree of reproducibility were obtained for the materials which underwent contraction, and also for most of those which showed expansion. However, some difficulty was experienced with vitrain of maximum swelling properties, as expansion was so great in some cases that the tube was of insufficient length to accommodate the coke. For these vitrains, which contained 85% to 88% carbon and gave expansions of more than 100%, a depth of 0·3 inch of the granular material was filled into the tube before carbonisation, enabling expansion results to be obtained. This introduced a variation in the conditions of carbonisation for a limited number of the strongly swelling vitrains, but their expansion was so great compared with all other members of the metamorphic series that discrepancies due to varied experimental conditions could not materially influence the general significance of results obtained.

After each test, the carbonised product was carefully removed from the tube and observations made as to its character. It was then crushed, where necessary, and sieved and graded as described earlier in the preparations of the vitrains. Some interesting features were noted in comparing the general nature of the granular samples of the vitrains with that of their carbonised products, and these observations are described later in this paper.

The residues from the carbonisation tests were saturated in preparation for determination of maximum inherent moisture, by boiling the granular material in water under reflux for one hour and then allowing it to stand in air-free water, in a tightly sealed test tube, for at least four days. Maximum inherent moisture was then determined in the same way as for the saturated vitrains. Behaviour of the carbonised products during removal of adherent moisture was exactly similar to that of the vitrains, except for cokes of strongly swelling vitrains which took a longer time to reach apparent dryness. Results for moisture determinations of the carbonised products (see Table 2) could be reproduced with the same degree of accuracy as those obtained for vitrains.

NOTES ON CHEMICAL PROPERTIES OF VITRAINS.

The selected materials range in carbon from 51·3% for a Pleistocene peat to 97·3% for the Rhode Island anthracite : the highest carbon determined for an Australian vitrain being 91·5%, which was obtained for a semi-anthracite from Mittagong, N.S.W. In this instance, anthracitisation is directly attributable to local igneous alteration by a sill. In general, there is a notable lack of true anthracite coals in Australian coalfields, due to the absence of widespread igneous alteration or folding of the Permian coal measures.

Hydrogen values obtained for the complete series vary between limits of 2·0% and 7·3%. Raistrick and Marshall found that a series of vitrains from American coals ranged from 5·1% to 6·0% hydrogen. Their materials, varying from 55% to 90% carbon, were all from American coalfields, whereas materials used in the present work came from widely scattered areas in different countries.

In a more detailed study of the constitution of vitrains from American coals, Marshall (1943) obtained results which present an interesting comparison with hydrogen values obtained for Australian vitrains. For the American series with a variation of 55·6% to 87·8% carbon it was found that hydrogen varied within limits of 4·6% and 6·0%. These figures were obtained from analyses of sixty-six samples of vitrain and it was noted that 95·5% of all members of the series had a hydrogen content between 5% and 6%. Hydrogen determined for Australian vitrains in the present investigation varies between limits of 4·4% and 6·8% for a similar carbon range (51·3% to 88·0%). This group contains thirty-four different samples but only 61·8% of these vitrains had a

hydrogen content between 5% and 6% ; that is, a little more than half of the materials conformed to the variation determined by Marshall. Of the remainder, 29·4% had a hydrogen content of less than 5%, and the rest (8·8% of the series) had more than 6% hydrogen. Considering hydrogen content of Australian vitrains of all ranks, from 51·3% to 91·6% carbon, limits of hydrogen range from 3·3% to 6·8%, with only 58% of the vitrains analysed having a hydrogen content between 5% and 6% ; from which it would appear that the proportion of hydrogen in Australian vitrains may vary over a considerably wider range of values than that determined for American vitrains. This contrast in proportions of hydrogen in vitrains from coals of the Northern and Southern Hemispheres may be the result of different environmental conditions of coalification or it may indicate fundamental differences in the nature of the original coal-forming constituents. It suggests that the plant material from which Australian coals were derived was of greater, or different, variety to that which gave rise to the American coals.

Standard proximate analyses at 925° C. (see Table 1) of all members of the vitrain series confirms the well-established continuous variation of volatile content with rank. Actual values range from a minimum of 3·8% for the Rhode Island material to a maximum of 87·7% for a German peat. Volatile yields calculated from low-temperature carbonisation of a selected number of the vitrains shows the same general increase in volatiles with increase in rank. However, actual values obtained for volatiles were much lower at the lower temperature. In plotting volatiles at 925° C. and at 600° C. against carbon, two distinct zones are obtained, the volatiles determined at the higher temperature falling in the upper zone. An examination of the differences in volatile contents obtained at the different temperatures shows that the increase in values at the higher temperature is not constant, and has no relationship to the rank of the vitrain from which it was obtained. Actual increases vary between limits of 3·9 and 18·3%.

Ash values for the vitrains are generally low, ranging from 0·1% to 6·0% with an overall average of 2·8% for the whole series ; exceptions are the high ash values obtained for the Rhode Island anthracite and the Currabubula (N.S.W.) material, neither of which, however, was included in the preliminary acid washings. The anthracite, as already mentioned, cannot be regarded as a pure vitrain and the Currabubula material came from an area closely associated with igneous intrusion, producing an exceptionally high-ash coal.

NATURE OF THE CARBONISED PRODUCTS.

The carbonised residues of the granular vitrains fall into two distinct groups, which for the purpose of this paper will be referred to as *chars* and *cokes*. The chars are the non-coherent residues and the cokes are the coherent residues. Since all members of the metamorphic series are represented the nature of the carbonised residues varies considerably. Cokes are formed from vitrains of 79% to 89% carbon. Where carbon of the vitrain lies between 83% and 89%, a completely fused coke is formed in which no trace remains of the original individual grains. Two types of completely fused coke are recognisable and are described as *bubbly fused coke* and *dense fused coke*. The former is a coarsely porous or intumesced coke and the latter is more finely porous and rather compact. Their formation does not seem to depend on the carbon content within this particular carbon range, nor does it seem to be related to the actual percentage of volatiles. However, the formation of bubbly fused coke is directly related to bulk-volume changes on carbonisation and is probably associated with the plastic properties of the vitrain during thermal decomposition.

Where the carbon of the vitrain ranges between 79% and 83%, the form of the carbonised residue varies greatly, this being in the nature of a transition

zone between the chars and the cokes, both of which are represented. Cokes of this group are typically partly fused or granular with the original grains distinguishable though they have become rounded or globular. Two types of granular cokes are distinguished and described as *strongly coherent granular coke* and *weakly coherent granular coke*, the distinction, as the terms suggest, being based on the degree of coherency of the individual grains.

Chars are formed from vitrains of both higher and lower rank than those which produce cokes. The chars formed from vitrains of sub-bituminous or lower rank (i.e. 79% carbon or less) will be referred to as *low-rank chars*, and those formed from vitrains on the high-rank, or anthracite, side of the coking vitrains (i.e. higher than 89·2% carbon) will be termed *high-rank chars*. Both low-rank and high-rank chars are completely non-coherent but it will be seen later that they are further distinguished by differences in their ultra-fine structure. It was noted that chars formed from vitrains which were originally bright have a brighter lustre than the vitrains from which they were formed. This was observed in chars from vitrains of both sub-bituminous and anthracite rank. However, vitrains from the brown coals and peats, which are dull in their original water-saturated condition and vary in colour from brown to black, form dull, black chars.

RELATION OF BULK-VOLUME CHANGES ON CARBONISATION TO RANK.

Results of bulk-volume changes on low-temperature carbonisations of granular vitrain, under free-swelling conditions as described earlier in this paper, are recorded in Table 1. Values obtained for percentage expansion or contraction were plotted against carbon as rank index, as illustrated in Figure 1. All points on the graph fall within a zone of fairly constant width, with a maximum in the region of the coking coals. The relationship so obtained illustrates variation in bulk-volume changes with rank. Where carbon of the vitrain is less than 79%, or exceeds 89%, contraction in bulk-volume takes place, with the formation of a char. Between 79% and 83% carbon, either contraction or expansion may take place, and where carbon lies between 83% and 89% expansion only is obtained.

On the low-rank side of the graph there is a suggestion of a zonal minimum in the region of 67% carbon. This corresponds very closely with the maximum in the moisture-rank relationship recorded by Dulhunty (1948) for the same vitrains, and it is suggested by that author that the maximum in moisture probably corresponds with the maximum degree of colloidal development attained during coalification. However, while the zonal maximum (Fig. 1) corresponds approximately with maximum colloidal development in the vitrain, the greatest contraction recorded (Vitrain No. 453) falls towards the low-rank side of the zonal minimum. This vitrain, having a contraction of 66%, is a peat wood from Haltern, Germany. It is perhaps significant that it undergoes least irreversible change on drying, and that maximum irreversible changes on drying are recorded (Dulhunty, 1948) for those materials falling in the region of the zonal minimum.

Vitrains of carbon content between 83% and 89% all show expansion on carbonisation, and the peak of this section of the zone lies at approximately 86% carbon. Expansion for these materials ranges from 21% to 598%, and the carbonised residues are all completely fused. There would seem to be some relationship between degree of expansion and maximum inherent moisture of the original vitrain. That the coking coals corresponded with the minimum in the moisture-carbon curve has long been recognised and more recently illustrated by Dulhunty (1948). From the results recorded in this paper (Fig. 1), it may be noted that for points lying towards the maximum of the expansion-carbon zone, where expansion values exceed 300%, moisture of the vitrains is
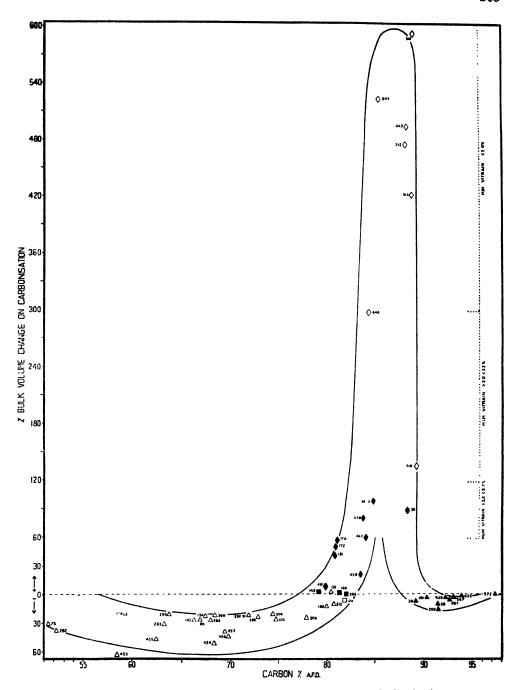
Fig. 1.—Relation of Rank to Bulk-Volume Changes on Carbonisation.
(For key to symbols see Fig. 2.)

2% or less. Where expansion exceeds 120% but not 300%, moisture values lie between 2% and 3·2%, and where expansion is greater than 60% but does not exceed 120%, moisture ranges between 3·2% and 5·7%. At the same

time, vitrains for which expansion values exceed 120% form bubbly fused cokes, and where expansion lies between 60% and 120%, dense fused cokes are formed.

In the 79% to 83% carbon group, where both expansion and contraction values are recorded, the carbonised residues are of various types. One vitrain (No. 288) of this group exhibits no change in bulk-volume on carbonisation. In this particular instance, tendencies to contract or expand are apparently compensating, although considerable changes occur in the ultra-fine structure of the material as will be illustrated later in this paper. Similar properties on carbonisation are also exhibited by the graphitic material, No. 572.

Considering again the chars formed from vitrains on both the high-rank and low-rank sides of the coking vitrains it was noted that in the case of the low-rank chars contraction in every instance exceeded 15%, while for the high-rank chars contraction did not exceed 15%.

In experiments designed to test the relation of free-swelling index to expansion of coal in experimental coke ovens for a series of coals ranging from low-volatile to high-volatile bituminous in rank, Selvig and Ode (1946) recorded measurements of percentage contraction and expansion on carbonisation. However, it was not possible to correlate their work with results obtained from vitrains of this series of similar rank, as materials used were pulverised rather than granular, and temperature ranges were not recorded for the experiments.

Cannon, Griffith and Hirst (1943) in their work on carbonisation of coals, also recorded measurements of contraction and expansion obtained on carbonising powdered coal which they related to heat of wetting phenomena. However, conditions of carbonisation were not comparable with those used in this work: time-temperature conditions were similar, but pulverised coal was used rather than granular vitrain and expansion and contraction measurements were not obtained under free-swelling conditions.

CHANGES IN PORE STRUCTURE IN VITRAIN ON CARBONISATION AND
RELATION TO RANK.

As described earlier in this paper, maximum inherent moisture determinations were carried out on the carbonised residues of all vitrains in the series (see Table 2). In the case of vitrain, maximum inherent moisture depends on the natural condition of the micelle structure determined by metamorphic evolution in the earth's crust. Maximum inherent moisture of the carbonised product depends on the effects of carbonisation, but in each case it is presumably a measure of something closely related to the total volume of openings forming part of the ultra-fine structure, and small enough to lower the vapour pressure of water.

No definite relationship was established between maximum inherent moisture of the carbonised product and carbon of the vitrain from which it was formed. In many instances the moisture in the carbonised residue exceeded that of the corresponding vitrain, and in other instances was lower. It was found, however, that the difference between the moisture of vitrain and its carbonisation products is closely related to carbon content, or rank, of the vitrain. To illustrate this, the numerical difference between the moisture values for the vitrain and its carbonised product was expressed as a percentage of the moisture of the vitrain. Where moisture of the carbonised residue exceeded that of the vitrain, the increase was expressed as a positive value, and conversely, a decrease was expressed as a negative value (see Table 2). This percentage increase or decrease in moisture was then plotted against carbon determined for the original vitrain. A well-defined zonal relationship was established (see Fig. 2), the form of the zone being illustrated by lines

TABLE 2.

Maximum Inherent Moisture of Vitrains and Their Carbonisation Products.

Spec. No.	Percentage Carbon A.F.D. Basis.	Percentage Maximum Inherent Moisture. Dry Basis.		Actual Actual Difference.	Percentage Increase or Decrease.
		Vitrain.	Carbonised Product.		
572	97·3	3·5	4·0	+0·5	+14·3
622	93·9	5·1	4·6	—0·5	—9·8
567	93·0	4·1	4·8	+0·7	+17·1
497	92·7	2·3	4·6	+2·3	+100·0
525	92·3	4·7	6·1	+1·4	+29·8
208	91·6	3·2	6·8	+3·6	+112·5
28	91·5	3·7	4·7	+1·0	+27·0
161	90·3	3·9	6·2	+2·3	+59·0
36	89·2	5·9	6·9	+1·0	+17·0
310	89·2	3·9	13·1	+9·2	+235·9
314	88·9	2·0	4·7	+2·7	+135·0
313	88·8	1·8	4·7	+2·9	+161·0
30	88·3	3·2	29·8	+26·6	+831·3
443	88·1	1·9	5·7	+3·8	+200·0
312	88·0	1·8	6·8	+5·0	+277·7
644	85·3	2·0	5·5	+3·5	+175·0
347–348	84·8	3·9	4·2	+0·3	+7·7
646	84·2	2·6	5·7	+3·1	+119·2
460	84·1	5·7	10·4	+4·7	+82·5
458	83·7	3·9	6·0	+2·1	+53·8
459	83·4	4·7	12·8	+8·1	+172·3
288	82·0	12·8	35·9	+23·1	+180·5
124	81·9	18·2	16·2	—2·0	—11·0
169	81·3	5·4	17·5	+12·1	+224·1
174	81·0	3·9	14·5	+10·6	+271·8
172	80·9	6·0	35·3	+29·3	+488·3
181	80·8	6·4	36·6	+30·2	+471·9
212	80·7	6·8	7·3	+0·5	+7·4
138	80·3	15·3	25·8	+10·5	+68·6
186	80·0	9·9	19·1	+9·2	+93·0
461	79·8	5·7	6·7	+1·0	+17·5
143	79·1	4·3	33·5	+29·2	+680·0
209	77·9	21·1	8·6	—12·5	—59·2
317	76·6	25·4	9·7	—15·7	—61·8
120	74·8	25·5	9·5	—16·0	—62·8
304	74·5	64·9	12·7	—52·2	—80·4
456	69·8	82·8	11·7	—71·1	—85·9
457	70·5	60·3	14·0	—46·3	—76·8
88	68·9	76·3	16·6	—59·7	—78·4
454	68·3	93·3	10·5	—82·8	—88·7
136	67·4	116·0	15·3	—100·7	—86·8
455	62·5	68·0	10·1	—57·9	—85·2
104	59·2	61·0	21·6	—39·4	—64·6
453	58·4	38·6	24·2	—14·4	—37·3

drawn at the approximate margins of the areas occupied by the points on the graph. This zone represents relationship of rank to moisture change on carbonisation.

All low-rank materials, that is vitrain of 79% carbon or less, show a decrease in moisture on carbonisation. At the low-rank extreme, a decrease in moisture of 37·3% is recorded for a peat wood of 58·4% carbon. As rank increases, the percentage decrease in moisture becomes greater till a zonal minimum is reached

at approximately 68% carbon.   With further increase in rank the zone gradually
rises, and at 79% carbon it becomes almost vertical, and all vitrains at this rank
or higher show, with two minor exceptions, an increase in moisture on carbon-
isation.   Between approximately 79% and 90% carbon there is a well-defined
maximum, the peak of which is probably situated at about 86% carbon.   Where
carbon lies between 79% and 82%, that is, for vitrains of bituminous rank, the
increase in moisture may be as much as 832%, or as little as 7·4%.   A sharp
reduction in moisture increase occurs at 90% carbon, and towards the anthracite
end of the zone, increase in moisture does not exceed 115% and gradually
lessens as carbon approaches 100%.

        An interesting comparison may be made in the form of this zone and that
obtained by Dulhunty (1948) for the maximum inherent moisture-carbon
relationship of the same vitrains.   The maximum in the moisture-carbon
curve at 68% carbon, corresponds exactly with the zonal minimum in the
relationship of rank to moisture change on carbonisation.   However, the
apparent peak, at 86% carbon, of the zonal maximum in this relationship
(Fig. 2) is a little to the low-rank side of the minimum in the moisture-carbon
curve which falls at about 88% carbon.

        The zonal relationship of rank to moisture change on carbonisation is
closely allied in form to that established for the relationship of bulk-volume
change on carbonisation to rank (Fig. 1).   In both instances zonal minima are
established at 68% carbon and the peaks of the maxima are developed at 86%
carbon approximately.   Vitrains of 79% carbon and less show a decrease in
moisture on carbonisation and a contraction in bulk-volume.   Between 79%
and 83% carbon, with one exception, all materials show an increase in moisture,
but changes in bulk-volume may be either contraction or expansion.   Where
vitrains are of coking bituminous rank, that is, between 83% and 89% carbon,
maximum expansion is recorded and all vitrains of this group show an increase
in moisture on carbonisation.   An interesting feature in the comparison of
these relationships is the increase in moisture in vitrains of 89% carbon or more
all of which suffer contraction in bulk-volume on carbonisation.

        Earlier in this paper a distinction is drawn between low-rank and high-rank
chars.   The relationship of moisture change on carbonisation to rank shows
that a further distinction may be drawn on the basis of properties related to
the ultra-fine structure of the chars.   The carbonised residues of low-rank
vitrains all show a decrease in moisture exceeding 37%, while the high-rank
chars, with one exception, show an increase in moisture.   An increase in moisture
on carbonisation is also shown by any vitrain which produces a completely
fused coke.   From the illustration in Fig. 2 it will be seen that the greatest
increase in moisture is obtained for dense fused cokes, and not for bubbly fused
cokes which emphasizes that the bubbly structure is a macroscopic feature.

        It is interesting and perhaps significant to note that the formation of low-
rank chars is accompanied by a decrease in maximum inherent moisture whilst
the formation of high-rank chars involves an increase.   The plastic properties
of coking coals during carbonisation have long been recognised and in vitrain
undergoing plastic deformation it is not difficult to visualise the necessary
rearrangement of the ultra-fine structure required to give an increase in moisture
on carbonisation.   Yet moisture increases are obtained in the case of the high-
rank vitrains which do not undergo plastic deformation in the same way, but
produce a char in which the identity of the original individual particles is retained.

        From the study of heat of wetting and carbonisation, carried out by the
British Coal Utilisation Research Association (Cannon, Griffith and Hirst,
1943) on coals varying in rank from high volatile bituminous through to medium
volatile anthracites, it was concluded that the micelle structure, or something
related to it, persists throughout carbonisation.   It was also concluded that
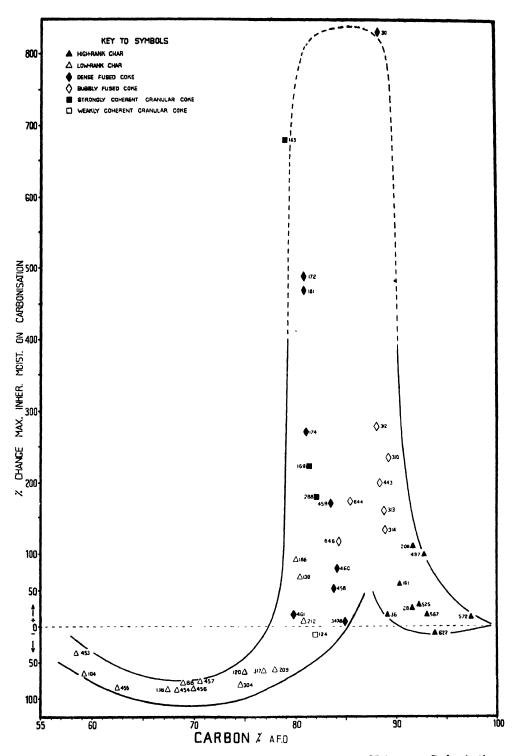
Fig. 2.—Relation of Rank to Per Cent. Change in Maximum Inherent Moisture on Carbonisation.

there is no great change in the internal surface area in so much that coals of small surface give carbonised products of small surface, and those with large surface give carbonisation products with large internal surface.

In so far as maximum inherent moisture determinations may be considered a measure of total internal volume of the coal substance (King and Wilkins 1943), then broadly the effects of carbonisation on the internal volume of the vitrains are as follows :

    (1) Volume decreases if the vitrain contains less than 79% carbon, or more significantly perhaps, if the material has not attained that critical stage in the process of coalification (Dulhunty, 1948) beyond which irreversible changes on drying do not take place.

    (2) Volume increases where carbon of the vitrain exceeds 79%, i.e. vitrain coalified beyond the stage at which irreversible changes take place on drying.

In the first case, carbonisation of the low-rank coals is accompanied by considerable loss of substance due to devolatilisation, and materials of this rank do not undergo plastic deformation during the process of carbonisation which produces a char. Reduction in internal volume then may be satisfactorily accounted for by the increased areas of contact between the micelle (with corresponding decrease in inter-micelle spaces) as suggested by Bangham (1943) and Bangham and Maggs (1943) to be the result of carbonisation. At the same time, these vitrains suffer a decrease in bulk-volume under free-swelling conditions of carbonisation.

The second group includes both the coking vitrains and those which give high-rank chars. The former give very great increases in internal volume, particularly vitrains from which dense fused cokes are formed. If, as heat of wetting determinations, carried out at various stages during the carbonisation of bituminous and anthracitic coals, and electrical conductivity measurements, would seem to so clearly indicate, the micelle structure or something related to it persists throughout carbonisation, it is difficult to account for the very large increases in internal volume recorded here for vitrains of similar rank and carbonised under similar conditions. The suggestion is offered that a new or supplementary pore structure is developed, dependent on the nature and rate of evolution of the volatiles and the degree of plasticity during carbonisation. In this structure the pores may be of such dimensions as to be inaccessible to the methanol molecule used in heat of wetting-surface area determinations, but accessible to the smaller water molecule used to measure internal volume. Alternatively, it is suggested that the original pore structure almost entirely disappears, being replaced by pores of greater radii which would increase internal volume but not internal area. That such a structure could result from gaseous emanations through a plastic medium during carbonisation is a possibility for consideration in the case of the coking vitrains, or those exhibiting intumescence, but it does not satisfactorily account for increases in internal volume obtained for vitrains producing high-rank chars. The latter do not undergo plastic deformation during carbonisation and volatile evolution is relatively insignificant ; moreover, a decrease in *bulk-volume* accompanies an increase in *internal volume* for the high-rank chars. The elucidation of these apparent anomalies offers an interesting problem for further research.

preparation of the paper. It is also wished to acknowledge generous cooperation of the Australian Coal Industry in obtaining materials for this investigation. Research facilities were provided by funds from the Commonwealth Research Grant to the University of Sydney.

BIBLIOGRAPHY.

Bangham, D. H., 1943. Proc. Conference on Ultra-fine Structure of Coals and Cokes. Brit. Coal Util. Res. Ass. H. K. Lewis and Co. Ltd., London, p. 18.

Bangham, D. H., and Maggs, F. A. P., 1943. *Ibid.*, p. 118.

Cannon, C. G., Griffith, M., and Hirst, W., 1943. *Ibid.*, p. 131.

Dulhunty, J. A., 1947. THIS JOURNAL, 81, 60.

————————— 1948. THIS JOURNAL, 82, 286.

Himus, G. W., 1946. Fuel Testing. Leonard Hill, Ltd., London.

King, J. G., and Wilkins, E. T., 1943. Proc. Conference on Ultra-fine Structure of Coals and Cokes. Brit. Coal Util. Res. Ass. H. K. Lewis and Co. Ltd., London, p. 46.

Marshall, C. E., 1943. *Fuel*, 22, 6, 140.

Raistrick, A., and Marshall, C. E., 1939. The Nature and Origin of Coal and Coal Seams. The English Universities Press Ltd., London, p. 229.

Selvig, W. A., and Ode, W. H., 1946. United States Bureau of Mines Report of Investigations, No. 3989.

SUMMARY.

Vitrains of all ranks from the Southern Hemisphere show greater variation in hydrogen content than those from the Northern Hemisphere, suggesting differences in original plant materials. Volatile yields at 920° C. exceed those at 600° C. by a variable amount which cannot be related to rank. A zonal relationship exists between rank and bulk-volume changes on carbonisation with a minimum at 67% carbon and a maximum at 86% carbon. A similar relationship was established between rank and differences in capillary-held moisture of vitrain and its carbonisation products. These relationships indicate that vitrains of 79% carbon or less produce chars, or non-coherent residues, showing an overall contraction in bulk-volume exceeding 15% and holding less capillary-condensed moisture than the original vitrain. Where carbon of the vitrain is 79% and does not exceed 89·2%, a coke is formed which may show either contraction or expansion in bulk-volume but in which capillary-condensed moisture exceeds that of the original vitrain. A char is also formed from vitrains of 89·2% carbon or more, in which overall contraction in bulk-volume does not exceed 15% and in which the amount of capillary-condensed moisture exceeds that of the original vitrain.

THE AUSTRALIAN SOCIAL SERVICES CONTRIBUTION AND INCOME TAX ACTS, 1949.

By H. MULHALL.

CONTENTS.

I.

Professor H. S. Carslaw has examined in a series of papers the graduation of Australian taxation on individual incomes from the introduction of uniform taxation in 1942 to the Social Services Contribution and Income Tax Acts of 1947 which were relevant to the year ending June 30th, 1948. Since the appearance of his last paper (Carslaw, 1948) there have been two further reductions in taxation. It is now proposed to set out for the most recent Act the analysis given by Professor Carslaw for the Act of 1947. His notation is retained; the amount of tax and/or contribution on an income of £x is denoted by T pence.

The rate of tax on this income is denoted by $R\left(=\dfrac{T}{x}\right)$ with, if required, a suffix, say R_1 or R_2. The rebatable amount on the income is denoted by £A.

II.

The basic rate of contribution applying to a taxpayer entitled to no rebates is given by the formula

$$R_1 = 3 + \frac{3}{80}(x - 100), \text{ when } x \leqslant 500.$$

The maximum rate of 18 pence is reached at $x = 500$.

The amount of contribution payable is thus

$$T = x\left[3 + \frac{3}{80}(x - 100)\right].$$

The contribution commences at $x = 105$, but there is a proviso that no person shall pay a contribution greater than half the excess of his income over £104.

For taxpayers entitled to rebates on account of dependents, medical expenses, etc., the concessional rate is given by the formulæ

$$R_2 = \frac{3x - A}{100} \text{ when } x - A < 100$$

$$= 3 + \frac{3}{80}(x - A - 100) \text{ when } 100 < x - A < 500.$$

$$= 18 \text{ when } x - A > 500.$$

When using these formulæ it should be noted that there is a special rebate for a taxpayer whose income does not exceed £350 and who has any dependents. This rebate is £50 when the income does not exceed £250, diminishing by £1 for every £2 by which the income exceeds £250, so that it vanishes at £350.

The following list shows the incomes at which liability to Social Services Contribution begins and those at which the maximum rate of 18 pence in the £ is reached.

	£
Single person	105–500
Person with dependent wife	201–650
Person with dependent wife and one child	284–750
Person with dependent wife and two children	318–800
Person with dependent wife and three children	351–850
Person with dependent wife and four children	401–900
Person with dependent wife and five children	451–950

III.

This section deals with Income Tax as distinct from Social Services Contribution, which must, of course, be added to the amounts calculated from the formulæ which follow to give the total amount payable. The formulæ refer to taxpayers entitled to no rebates.

Earned Income.

(a) When $x \leqslant 500$,

$$T = 0.$$

(b) When $500 < x \leqslant 1000$,

$$T = (x - 500)\left[18 + \frac{24}{1000}(x - 500)\right]$$

$$= \frac{24}{1000}x^2 - 6x - 3000.$$

(c) When $1000 < x \leqslant 2000$,

$$T = 15 \times 1000 + (x - 1000)\left[42 + \frac{2}{100}(x - 1000)\right]$$

$$= \frac{2}{100}x^2 + 2x - 7000.$$

(d) When $2000 < x \leqslant 5000$,

$$T = 38 \cdot 5 \times 2000 + (x - 2000)\left[82 + \frac{1}{100}(x - 2000)\right]$$

$$= \frac{1}{100}x^2 + 42x - 47000.$$

(e) **When** $5000 < x \leqslant 10,000$,

$$T = 82 \cdot 6 \times 5000 + (x - 5000)\left[142 + \frac{2}{1000}(x - 5000)\right]$$

$$= \frac{2}{1000}x^2 + 122x - 247,000.$$

(f) **When** $x > 10,000$,

$$T = 117 \cdot 3 \times 10,000 + 162(x - 10,000).$$

Income from Property.

(a) **When** $x \leqslant 350$,

$$T = 0.$$

(b) **When** $350 < x \leqslant 500$,

$$T = (x - 350)\left[7 \cdot 75 + (x - 350)\frac{5}{1000}\right]$$

$$= \frac{5}{1000}x^2 + 4 \cdot 25x - 2100.$$

(c) **When** $500 < x \leqslant 1000$,

$$T = 2 \cdot 55 \times 500 + (x - 500)\left[28 + \frac{3}{100}(x - 500)\right]$$

$$= \frac{3}{100}x^2 - 2x - 5225.$$

(d) **When** $1000 < x \leqslant 2000$,

$$T = 22 \cdot 775 \times 1000 + (x - 1000)\left[58 + \frac{22}{1000}(x - 1000)\right]$$

$$= \frac{22}{1000}x^2 + 14x - 13,225.$$

(e) **When** $2000 < x \leqslant 5000$,

$$T = 51 \cdot 3875 \times 2000 + (x - 2000)\left[102 + \frac{8}{1000}(x - 2000)\right]$$

$$= \frac{8}{1000}x^2 + 70x - 69,225.$$

(f) **When** $5000 < x \leqslant 10,000$,

$$T = 96 \cdot 155 \times 5000 + (x - 5000)\left[150 + \frac{12}{10000}(x - 5000)\right]$$

$$= \frac{12}{10000}x^2 + 138x - 239,225.$$

(g) **When** $x > 10,000$,

$$T = 126 \cdot 0775 \times 10,000 + 162(x - 10,000).$$

IV.

It will be noticed that all the amounts in Section III (except for $x > 10,000$) are expressed in the form $ax^2 + bx + c$. The total amount payable (Income Tax plus Social Services Contribution) is also expressible in this form. Following

Carslaw's notation, if $T(x)$ denote the amount payable on an income of £x, the xth £ pays an amount $T(x) - T(x-1)$, an expression of the form $a(2x-1)+b$. It is this increment which interests the taxpayer concerned about the amount of tax payable on additional income.

Earned Income.

There is no income tax on incomes not exceeding £500 ; the amount of contribution payable is

$$x\left[3+\frac{3}{80}(x-100)\right]$$

$$=\frac{3}{80}x^2-\tfrac{3}{4}x.$$

The xth £ therefore pays $\frac{3}{80}(2x-1)-\tfrac{3}{4}$ pence.   For example, at $x=400$ the

amount of contribution is 5700 pence ; the rate $\left(\dfrac{T}{x}\right)$ is $14\cdot25$ pence per £. The

401st £ pays $29\cdot2875$ pence.

When x exceeds 500, the Social Services Contribution remains 18 pence per £.   The total amount payable on an income of £x is thus

$$ax^2+bx+c+18x$$

the values of a, b, c being those given in Section II for the various income ranges. The amount payable on the xth £ is $[a(2x-1)+b+18]$ pence.   For any given range, these increments form an arithmetic progression with common difference $2a$.

Thus, the 501st £ pays $36\cdot024$ pence ; the common difference for the range is $0\cdot048$ and the 1000th £ pays $59\cdot976$ pence.

The 1001st £ pays $60\cdot02$ pence ; the common difference is $0\cdot040$ and the 2000th £ pays $99\cdot98$ pence.

The 2001st £ pays $100\cdot01$ pence ; the common difference is $0\cdot020$ and the 5000th £ pays $159\cdot99$ pence.

The 5001st £ pays $160\cdot002$ pence ; the common difference is $0\cdot004$ and the 10,000th £ pays $179\cdot999$ pence.

The 10,001st £ pays 180 pence.   This is the maximum rate.

It is interesting to note that the 3001st £ pays $120\cdot02$ pence.   For a taxpayer without dependents it is only on income in excess of £3000 that more than half of every additional pound is paid out in tax.

Income from Property.

For property incomes, tax begins at £350, before the Social Services Contribution has reached the maximum rate.   From the expressions for Tax and Contribution, the following formula for the total amount payable is obtained

$$\frac{42\cdot5}{1000}x^2+3\cdot5x-21,000 \qquad 350<x\leqslant500.$$

The 351st £ pays $33\cdot2925$ pence ; the common difference is $0\cdot085$ and the 500th £ pays $45\cdot9575$ pence.

For incomes in excess of £500 the calculation of the increment is carried out in the same way as for earned income, the values of a and b corresponding

to a given value of x being ascertained from the formulæ of Section III. For example, if $1000 < x < 2000$, $a = 0 \cdot 022$, $b = 14$. The 1001st £ pays a total of $58 \cdot 022 + 18 = 76 \cdot 022$ pence ; this increment increases by $0 \cdot 044$ pence per £ and the 2000th £ pays $119 \cdot 978$ pence. For property incomes the increment exceeds 10/– in the £ when x exceeds 2000. The maximum rate of 180 pence is again reached at incomes of £10,000, but the approach to this rate is more rapid than for earned income.

V.

Figure 1 shows the total amount (Tax and Contribution) by each £ of income received in the year ending June 30th, 1950, for a taxpayer entitled to no rebates. The procedure followed is that given by Carslaw.

If the total amount payable has the form $ax^2 + bx + c$, the amount. paid by the xth £ has been shown to be $[a(2x - 1) + b]$ pence. Thus the line $y = 2ax + b$ has for the ordinate at $x - \frac{1}{2}$ the amount of tax on the xth £. For earned income
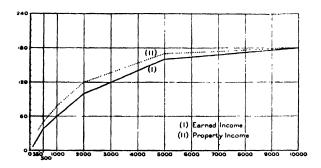
Fig. 1.

the graph will be made up of line segments corresponding to the ranges (a) to (f) of Section III. We shall assume $x > 105$. The equations of the lines are given below.

(a) $x \leqslant 500$ $\qquad y = \frac{3}{40}x - \frac{3}{4}$

(b) $500 < x < 1000$ $\qquad y = \frac{48}{1000}x + 12$

(c) $1000 < x < 2000$ $\qquad y = \frac{40}{1000}x + 20$

(d) $2000 < x < 5000$ $\qquad y = \frac{20}{1000}x + 60$

(e) $5000 < x \leqslant 10,000$ $\qquad y = \frac{4}{1000}x + 140.$

When $x > 10,000$ the constant maximum rate is given by $y = 180$.

Similarly, the lines making up the graph relevant to Property Income are :

(a) $x \leqslant 350$ $\qquad y = \frac{75}{1000}x - \frac{3}{4}$

(b) $350 < x < 500$ $\qquad y = \frac{85}{1000}x + 3 \cdot 5$

(c) $500 < x < 1000$ $\qquad y = \frac{60}{1000}x + 16$

(d) $1000 < x < 2000$ $\qquad$ $y = \dfrac{44}{1000}x + 32$

(e) $2000 < x < 5000$ $\qquad$ $y = \dfrac{16}{1000}x + 88$

(f) $5000 < x < 10{,}000$ $\qquad$ $y = \dfrac{2 \cdot 4}{1000}x + 156$

(g) $\qquad x > 10{,}000$ $\qquad$ $y = 180.$

It will be observed that there is an irregularity in the graph describing the amount payable on property income. This results from the commencement of Income Tax at $x = 350$, before the Contribution rate has reached its maximum value.
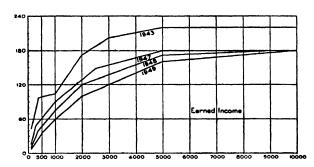
Fig. 2.
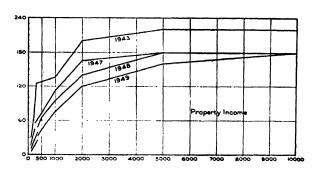
Fig. 3.

Figures 2 (Earned Income) and 3 (Property Income) compare the rates prevailing in 1943 (the year of maximum taxation), 1947, 1948 and 1949. Figure 2 shows that for incomes up to £1000 per annum it is no longer true that incentive to increase output is destroyed by the excessive taxation on additional earnings (overtime, etc.), the additional tax, even for a taxpayer without dependents, being always less than five shillings in the £.

REFERENCE

Carslaw, H. S., 1947.   The Australian Social Services Contribution and Income Tax Acts, 1947. *The Economic Record*, pp. 3-11.   References to papers on the earlier Acts are given in this paper.

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STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART I. TETRAMMINE PLATINUM (II) FLUORIDES.

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A survey of the literature on platinum and fluorine indicates very little is known on the chemistry of platinum fluorides. Platinum (II) and platinum (IV) fluorides have been reported (Mellor, 1937). Fluoroplatinates (IV) of sodium, potassium and ammonium have also been prepared (Mellor, 1937), K_2PtF_6 (Schlesinger and Tapley, 1924) being a pale yellow crystalline compound sparingly soluble in water, in which it is relatively stable. Among the platinum complexes, Hedin (1886) reported the possible existence of difluoro dipyridine platinum (II). $[Pt(NH_2OH)_4](HF_2)_2.2H_2O$ has also been prepared (Goremykin, 1944).

In this investigation the fluorides and hydrogen fluorides of the complex ion $[PtA_4]^{++}$ have been prepared ($A=NH_3$, C_5H_5N ; $2A=C_2H_4(NH_2)_2$). These are all colourless substances, crystallising in well-formed crystals from water or aqueous acetone, often with water of crystallisation, part of which is lost on drying over P_2O_5. They were all readily soluble in water, the solution of the hydrogen fluorides having a distinctly acid reaction and liberating CO_2 from carbonates. The ion $[PtA_4]^{++}$ was quite stable in the presence of excess hydrofluoric acid, and the salts could be evaporated with 46% acid at the boiling point without decomposition.

Hydrogen fluorides prepared by evaporation to dryness in this fashion yielded salts of the type $[Pt(NH_3)_4](HF_2)_2$. These salts were stable in a dry atmosphere but exposure to air resulted in the loss of HF, glass in the immediate vicinity being etched. The effect was greatest with the ethylenediamino and least with the pyridino compounds. Further, when $[Pt\{C_2H_4(NH_2)_2\}_2](HF_2)_2$ was dissolved in aqueous hydrofluoric acid solution and crystallised by the addition of acetone, the compound $[Pt\{C_2H_4(NH_2)_2\}_2]HF_2.F.H_2O$ was obtained, in which one HF_2^- anion had been replaced by a $F^-.H_2O$ group. The same tendency was probably operative in the case of the $[Pt(NH_3)_4](HF_2)_2$ salt. Whenever crystallised from aqueous acid solution by the addition of acetone, the compound contained less F than required by formula. It is possible that a continuous series of compounds, containing mixed anions, exist intermediate between $[Pt\{C_2H_4(NH_2)_2\}_2](HF_2)_2$ and $[Pt\{C_2H_4(NH_2)_2\}_2]\dfrac{F.H_2O}{HF_2}$, in which the H_2O is strongly held by the hydrogen bonds to the F^- anion, so that the HF_2^- can be replaced by F^- . . . H–O–H without alteration to the structure.

The stability of the complex ion towards hydrofluoric acid contrasts strongly with its behaviour towards other halogen acids. Thus it is well known that the addition of hydrochloric acid to $[Pt(NH_3)_4]Cl_2$ results in the formation of $[Pt(NH_3)_2Cl_2]$. That this difference cannot be attributed wholly to the fact that hydrofluoric acid is a comparatively weak acid is supported by the fact that $[Pt(NH_3)_4]I_2$ passes readily to $[Pt(NH_3)_2I_2]$ on boiling the aqueous solution.

Thus it must be assumed that the lack of reaction between $[Pt(NH_3)_4]^{++}$ and HF is due in some measure to the reluctance of Pt and F to form a covalent bond.

The stability of these compounds to heat is in process of investigation in order to compare with the general reaction of the type

$$[Pt(NH_3)_4]X_2 \xrightarrow{\triangle} [Pt(NH_3)_2X_2] + 2NH_3$$
$$X = Cl, \ Br, \ I.$$

Preliminary experiments on the behaviour of the cis and trans diammine bases, $[Pt(NH_3)_2(OH)_2]$ etc., with hydrofluoric acid have indicated anomalous results. The results of these experiments will be reported in later papers in this series.

EXPERIMENTAL.

(All operations involving fluorides were carried out in platinum or paraffin vessels. The hydrofluoric acid used was A.R. quality (General Chemical Co., U.S.A.) with analysis $0 \cdot 15\%$ H_2SiF_6 (max.).

Tetrammine Platinum (II) Hydrogen Fluoride.

$[Pt(NH_3)_4]Cl_2.H_2O$ was prepared ("Inorganic Syntheses", II, 250).

Found: Pt, $55 \cdot 6\%$; Cl, $20 \cdot 3\%$. Calculated: Pt, $55 \cdot 4\%$; Cl, $20 \cdot 1\%$.

$[Pt(NH_3)_4]Cl_2.H_2O$ ($0 \cdot 5$ g.) was converted to a solution of $[Pt(NH_3)_4](OH)_2$ with Ag_2O. After separation of AgCl and excess Ag_2O, the solution was acidified with excess HF, evaporated to near dryness on the water bath and finally dried in an air oven at about 70° C. until excess HF expelled. The residue was further dried *in vacuo* over $CaCl_2$ for several days. Under microscope, the compound consisted of clear, colourless quadrilateral plates with angles $\neq 90°$. The compound was readily soluble in water, the solution having a distinctly acid reaction. Yield, $0 \cdot 4$ g. On exposure to air the compound lost HF, glass in the vicinity being etched.

Found: Pt, $56 \cdot 9\%$; F, $21 \cdot 7\%$.

$[Pt(NH_3)_4](HF_2)_2$ requires Pt, $57 \cdot 2\%$; F, $22 \cdot 3\%$.

The method was varied by crystallising the salt from aqueous hydrofluoric solution with acetone. The compound crystallised in long thin needles.

Found (dried over P_2O_5): Pt, $57 \cdot 1\%$; F, $20 \cdot 3\%$.

Recrystallised aqueous HF+acetone, Pt, $57 \cdot 3\%$; F, $20 \cdot 5\%$.

Tetrammine Platinum (II) Fluoride 1·5 Hydrate.

$[Pt(NH_3)_4]Cl_2.H_2O$, $5 \cdot 0$ g., was converted to a solution of the corresponding hydroxide as before and the solution divided into two équal portions. One portion was converted to the solid hydrogen fluoride and the second portion then added. After evaporation the compound was crystallised by the addition of acetone. Recrystallised from aqueous acetone. Yield, $4 \cdot 1$ g. $[Pt(NH_3)_4]F_2.1\frac{1}{2}H_2O$ was readily soluble in water, the solution having an alkaline reaction (litmus). From aqueous acetone the compound was obtained in very fine white microcrystals. On heating at 100° C. only $1H_2O$ is lost, the remaining $\frac{1}{2}H_2O$ being held strongly in the compound, probably by hydrogen bonds to the fluoride ion.

Found (on air-dry material): Pt, $59 \cdot 9\%$; F, $11 \cdot 1\%$; H_2O, $5 \cdot 8\%$ (loss in one hour at 100° C.).

$Pt(NH_3)_4F_2.1\frac{1}{2}H_2O$ requires Pt, $59 \cdot 5\%$; F, $11 \cdot 6\%$. Loss for $1H_2O$, $5 \cdot 5\%$.

Tetrapyridine Platinum (II) Hydrogen Fluoride 6-Hydrate.

$[Pt(C_5H_5N)_4]Cl_2.3H_2O$ (Drew, Pinkard, Wardlaw and Cox, 1932) was recrystallised from aqueous acetone.

Found: Pt, $30 \cdot 7\%$; Cl, $11 \cdot 1\%$. Calculated: Pt, $30 \cdot 7\%$; Cl, $11 \cdot 1\%$.

3·0 g. were treated in the same manner as described for the corresponding tetrammino compound. From aqueous HF solution [Pt(C₅H₅N)₄](HF₂)₂.6H₂O crystallised in white opaque rectangular plates on the addition of acetone ; yield, 1·0 g. The compound was very soluble in water, the solution having a distinctly acid reaction. Over P_2O_5, $5\frac{1}{2}H_2O$ are lost, the remaining $\frac{1}{2}H_2O$ being lost on heating to 100° C. The dehydrated salt very slowly absorbs H_2O from the air. On exposure to air the salt slowly loses HF, this effect being less than with the corresponding tetrammino salt.

Found (on air-dry material) : Pt, 28·0% ; F, 10·7% ; H_2O, 14·1%, 14·2% (loss *in vacuo* over P_2O_5), 15·4% (loss in one hour at 100°).

[Pt(C₅H₅N)₄](HF₂)₂.6H₂O requires Pt, 28·0% ; F, 10·9%. Loss for $5\frac{1}{2}H_2O$, 14·2% ; loss for 6H₂O, 15·5%.

Tetrapyridine Platinum (II) Fluoride 9-Hydrate.

5·0 g. of the corresponding chloride were treated by the method employed for the corresponding tetrammino compound. From the aqueous solution [Pt(C₅H₅N)₄]F₂.9H₂O crystallised in clear colourless cubes and octahedra on the addition of acetone. Recrystallised from aqueous acetone. Yield, 3·3 g. The compound was readily soluble in water, giving a distinctly alkaline reaction with litmus paper. The salt readily loses 6H₂O on drying over P_2O_5. The trihydrate is stable to 100°, at which temperature decomposition is commencing, pyridine being lost and the residue turning yellow. The trihydrate rapidly takes up six moles of H_2O on exposure to air.

Found (air-dry material) : Pt, 27·6% ; F, 5·3% ; H_2O, 15·1%, 15·7% (loss ·*in vacuo* over P_2O_5).

[Pt(C₅H₅N)₄]F₂.9H₂O requires Pt, 27·4% ; F, 5·3%. Loss for 6H₂O, 15·2%.

Bis(ethylenediamine) Platinum (II) Hydrogen Fluoride.

Bis(ethylenediamine) platinum (II) chloride was prepared by the action of aqueous ethylenediamine on K₂PtCl₄, filtering the insoluble [Pt{C₂H₄(NH₂)₂}Cl₂] and dissolving in aqueous ethylenediamine. [Pt{C₂H₄(NH₂)₂}₂]Cl₂ crystallised on the addition of alcohol-acetone. Recrystallised from hot water.

Found : Pt, 50·5% ; Cl, 18·3%. Calculated : Pt, 50·5% ; Cl, 18·4%.

1·0 g. was converted at the corresponding hydroxide and the solution evaporated with excess HF in the same manner as described for the corresponding tetrammino compound. After evaporation on the water bath the residue was baked in an air oven at 110° C. Yield, 1·1 g. Examined under microscope, the material consisted of broken, jagged, colourless crystals. The compound was slightly deliquescent and readily soluble in water, the solution having a distinctly acid reaction. On exposure to air HF is readily lost, glass in the vicinity being badly etched.

Found (material dried over CaCl₂) : Pt, 49·5% ; F, 18·9%.

[Pt{C₂H₄(NH₂)₂}₂](HF₂)₂ requires Pt, 49·6% ; F, 19·3%.

Bis(ethylenediamine) Platinum II Fluoride Hydrogen Fluoride 1-Hydrate.

A solution of the hydrogen fluoride, prepared as above, in aqueous hydrofluoric acid, was crystallised by the addition of acetone. The compound crystallised in clear colourless rectangular plates. The dry compound gave an acid reaction with moist litmus paper.

Found (material dried over P_2O_5) : Pt, 49·8% ; F, 13·8%.

$[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]\dfrac{\text{F.H}_2\text{O}}{\text{HF}_2}$ requires Pt, 49·9% ; F, 14·5%.

Bis(ethylenediamine) Platinum (II) Fluoride 2-Hydrate.

5·0 g. of the chloride treated as described for the corresponding tetrammine compound. After concentration the compound was crystallised by the addition of acetone. Yield, 4·4 g. Recrystallised from aqueous acetone. Yield, 4·1 g. The compound which crystallised in clear

colourless quadrilateral plates with angles $\neq 90°$, was readily soluble in water to give an alkaline solution (litmus). Over P_2O_5, $1\frac{1}{2}H_2O$ are lost, the remaining $\frac{1}{2}H_2O$ being very strongly held.

Found (air-dry material): Pt, 49·6% ; F, 9·5% ; H_2O, 7·2%, 6·6% (loss over P_2O_5 no further loss on heating two hours at 140° C.).

$[Pt\{C_2H_4(NH_2)_2\}_2]F_2.2H_2O$ requires Pt, 50·1% ; F, 9·8% ; $2H_2O$, 9·3% ; $1\frac{1}{2}H_2O$, 7·0%.

Analyses.

Platinum analyses were made by igniting 0·1 g. of material in a platinum crucible. Fluorine was determined by boiling 0·1 g. material with excess aqueous ammonia until the odour of ammonia was faint and then by the standard method of adding sodium carbonate and pre-cipitating calcium carbonate and fluoride with calcium chloride. The separated material was ignited in a platinum crucible treated with excess acetic acid and evaporated to dryness on the water bath. The calcium fluoride was filtered, ignited and weighed. The calcium fluoride was converted to calcium sulphate as a check. Finally the calcium sulphate was dissolved in diluted hydrochloric acid and a small quantity of platinum (usually <0·5 mg.) was filtered, ignited and weight deduced from calcium fluoride and calcium sulphate. Good agreement between calcium sulphate and calcium fluoride weight was obtained in each case. The fluoride percentage was not corrected for small solubility of calcium fluoride in the water used for washing the precipitate. It is estimated that in compounds with 20% and 10% F. the result would probably be low by 2% and 4% respectively.

SUMMARY.

The preparation of the fluorides and hydrogen fluorides of $[Pt(NH_3)_4]^{++}$, $[Pt(C_5H_5N)_4]^{++}$, and $[Pt\{C_2H_4(NH_2)_2\}_2]$ are described. They are all well defined, colourless crystalline compounds, readily soluble in water. Evidence was obtained that compounds with mixed fluoride and hydrogen fluoride anions exist.

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REFERENCES.

Drew, Pinkard, Wardlow and Cox, 1932. *J.C.S.*, 1004.
Goremykin, 1944. *Bull. Acad. Sci. U.R.S.S.*, 105.
Hedin, 1886. Om Pyridinens platinabaser, Lund, 1886.
Mellor, 1937. Inorganic and Theoretical Chemistry, **16**.
Schlesinger and Tapley, 1924. *J.A.C.S.*, **46**, 276.

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PART IV

INVOLUTIONS ON A CONIC AND ORTHOGONAL MATRICES.

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(Communicated by Professor T. G. Room, F.R.S.)

Let s be a given non-degenerate conic in a plane π. Each point P of π (P not on s) determines an involutory self-transformation P of s and every such transformation is determined by a point of π not on s. (The identity will not be regarded as an involution here.) If a line through P meets s in points U, V we shall write $U\mathsf{P}=V$. If Q is any point of π and VQ meets s again in W, we write

$$U\mathsf{PQ}=V\mathsf{Q}=W.$$

It is clear that the operators P, Q, . . . form a multiplicative set which are fully associative; the product of any number of these operators is a projectivity which is not, in general, an involution. The involutory transformations of a conic form a subset, never a subgroup, of the group of transformations of the conic.

The aim of the first part of this paper is to discuss the conditions under which the product $\mathsf{A_1 A_2} . . . \mathsf{A_{n-1}}$ of a number of involutions is an involution $\mathsf{A_n}$. This is equivalent to the conditions that

$$\mathsf{A_1 A_2} . . . \mathsf{A_n}=\mathsf{I} \tag{1}$$

where I is the identical transformation.

The problem of inscribing a polygon $P_1 P_2 . . . P_n$ in s so that $P_i P_{i+1}$ passes through A_i ($A_1, . . ., A_n$ being n given distinct points) is known to have two solutions in general. [See, e.g., Salmon, 1850.] The condition that this problem have an infinity of solutions is obviously that the relation (1) above should hold.

For the case $n=2$ we see at once that $\mathsf{A_1 A_2}=\mathsf{I}$ if, and only if, $\mathsf{A_1}=\mathsf{A_2}$, i.e. $A_1=A_2$.

For $n=3$ we shall prove

Theorem 1. A necessary and sufficient condition that $\mathsf{A_1 A_2 A_3}=\mathsf{I}$ is that $A_1 A_2 A_3$ should be a self-polar triangle with respect to s.

Given that $\mathsf{A_1 A_2 A_3}=\mathsf{I}$, let $A_1 A_2$ meet s in points U, V. So $U\mathsf{A_1 A_2 A_3}=U$ and $U\mathsf{A_1 A_2}=U$; therefore $U\mathsf{A_3}=U$. I.e. A_3 lies on the tangent at U.

Similarly, we see that A_3 must lie on the tangent at V; and therefore A_3 is the pole of $A_1 A_2$.

Since $\mathsf{A_1 A_2 A_3}=\mathsf{I}$ and $\mathsf{A_3}^2=\mathsf{I}$ we have

$$\mathsf{A_3 A_1 A_2}=\mathsf{I}.$$

Therefore A_2 is the pole of $A_3 A_1$. Hence $A_1 A_2 A_3$ is a self-polar triangle.

The above proof breaks down if U and V coincide. In this case A_1, A_2, A_3 would have to be collinear on a tangent of s. It will be seen from Theorem 2 below that, if A_1, A_2, A_3 are collinear then $\mathsf{A_1 A_2 A_3}$ is always an involution and therefore cannot be the identity. Thus U and V would never coincide.

Conversely, if $A_1A_2A_3$ is a self-polar triangle, take any point P on s and let $PA_1=Q$, $QA_2=R$, $RA_1=S$, $SA_2=P'$. If A_2A_3 meets A_1P and A_1S in A_1' and A_1'' respectively, then

$$(A_1A_1',\ PQ)=-1=(A_1A_1'',\ RS).$$

Hence P and P' coincide and PR, QS must meet at A_3. Therefore $RA_3=P$ and so

$$PA_1A_2A_3=P \text{ or } A_1A_2A_3=I.$$

Corollary 1. The necessary and sufficient condition that **AB** be an involution is that A, B be conjugate points with regard to s.

Corollary 2. If the product of **A**, **B** and **C** in any one order is the identity then it is so for every order. (This is also obvious algebraically.)

For the case $n=4$ we shall prove :

Theorem 2. A necessary and sufficient condition that $A_1A_2A_3A_4=I$ is that $A_1, \ldots, A_4$ be collinear on a line l meeting s in U, V such that $(U,\ V)$, $(A_1,\ A_3)$, $(A_2,\ A_4)$ are pairs of an involution on l.

First, notice that if $PAB=P$ then A, B, P are collinear.

Given that $A_1 \ldots A_4=I$, let A_1A_2 meet s in U, V. Then $UA_1A_2=U$ and $VA_1A_2=V$.

But $A_1A_2=A_4A_3$; therefore $UA_4A_3=U$ and $VA_4A_3=V$. So A_3 and A_4 must lie on UV ; i.e., $A_1, \ldots, A_4$ are collinear. (The proof is still valid if U and V coincide.)

Now take any point P on s and let $PA_1=Q$, $QA_2=R$, $RA_3=S$. Therefore $SA_4=P$. Hence $(U,\ V)$, $(A_1,\ A_3)$, $(A_2,\ A_4)$ are pairs of an involution.

The converse result is easily proved.

Corollary. The product of three involutions **ABC** is an involution if, and only if, A, B, C are collinear.

Before treating the general value of n we shall require the following

Lemma A. Any projective transformation **L** of s into itself can be expressed as the product of two involutions and this can be done in ∞^1 ways.

For, let U, V be the self-corresponding points of the projectivity **L** and let $PL=Q$ where P is an arbitrarily chosen point of s. Take any point M on UV and let PM meet s again in R and RQ meet UV in N.

Now $PLNM=P$, and also

$$ULNM=U,\ VLNM=V.$$

Thus U, V, P are three distinct self-corresponding points of the projectivity **LNM** which must therefore be the identity.

Hence **L=MN**.

M was chosen arbitrarily on UV and N was then uniquely determined ; thus **L** is expressible as the product of two involutions in ∞^1 ways.

If the given projectivity is parabolic the theorem is still true but the above proof will need modification.

We now discuss our initial problem for a general value of $n(>4)$.

$A_1A_2 \ldots A_{n-2}$, being a projectivity, is, by the above lemma, expressible as the product of two involutions **MN**. Moreover, if U, V are the self-corresponding points of this projectivity, then M, N lie on UV.

T

The condition that

$$A_1 A_2 \ldots A_n = I$$

will therefore be the condition that

$$MNA_{n-1}A_n = I.$$

From Theorem 2 it follows that this is equivalent to the condition that A_{n-1} and A_n should lie in UV and that (U, V), (M, A_{n-1}), (N, A_n) be pairs of points in involution.

Since $A_1 \ldots A_{n-2} \neq I$ (we assume that $A_1 \ldots A_n$ contains no superfluous factors) it follows that there exist just two polygons of $(n-2)$ sides inscribed in s with their sides passing through $A_1, \ldots, A_{n-2}$ in order, U being the first vertex of one polygon and V the first vertex of the other.

We have thus proved

Theorem 3. A necessary and sufficient condition that ABC . . . PQ be an involution is that the point Q should lie on the line joining the self-corresponding points of the projectivity ABC . . . P.

The following deductions are immediate.

Corollary 1. The freedom of sets of points $A_1, \ldots, A_n$ such that $A_1 A_2 \ldots A_n = I$ is $2n-3$.

Corollary 2. If $A_1 A_2 \ldots A_n = I$ then the self-corresponding points of the transformation $A_{i+2}A_{i+3} \ldots A_n A_1 \ldots A_{i-1}$ are the intersections of $A_i A_{i+1}$ with s.

Corollary 3. If $A, B, \ldots, J, K$ be an odd number of points lying on a line l then AB . . . K is an involution. (The self-corresponding points of AB . . . J are the intersections of l with s.)

Algebraic Contents of the Results.

Taking the conic s in the form

$$x_0 : x_1 : x_2 = t_1^2 : t_0 t_1 : t_0^2$$

where (x_0, x_1, x_2) are homogeneous coordinates in the plane and (t_0, t_1) homogeneous parameters, the involutory self-transformation P of s determined by the point P (p_0, p_1, p_2) may be expressed thus :

$$\begin{pmatrix} t_0 \\ t_1 \end{pmatrix} = \begin{pmatrix} p_1 & -p_0 \\ p_2 & -p_1 \end{pmatrix} \begin{pmatrix} t_0^* \\ t_1^* \end{pmatrix}$$

where $p_0 p_2 - p_1^2 \neq 0$ since P does not lie on s. Writing

$$P = \begin{pmatrix} p_1 & -p_0 \\ p_2 & -p_1 \end{pmatrix} \tag{2}$$

we see that P is fully characterised by the (non-singular) matrix **P** which is called an involutory matrix. $[\mathbf{P}^2 = (p_0 p_2 - p_1^2)I.]$ In other words, a 2 by 2 matrix is involutory if, and only if, it is of the form (2).

The above theorems, obtained geometrically, yield at once the following algebraic results.

Theorem 4. The product of two involutory 2 by 2 matrices AB is an involutory matrix, if, and only if,

$$a_0 b_2 + a_2 b_0 - 2a_1 b_1 = 0,$$

where

$$A = \begin{pmatrix} a_1 & -a_0 \\ a_2 & -a_1 \end{pmatrix} \text{ etc.}$$

Theorem 5. The product of three 2 by 2 involutory matrices $\mathbf{ABC}$ is an involutory matrix if, and only if,

$$\begin{vmatrix} a_0 & a_1 & a_2 \\ b_0 & b_1 & b_2 \\ c_0 & c_1 & c_2 \end{vmatrix} = 0.$$

Theorem 6. Let $\mathbf{A}, \mathbf{B}, \ldots, \mathbf{J}, \mathbf{K}$ be a set of involutory 2 by 2 matrices and let $\mathbf{AB} \ldots \mathbf{J} = \mathbf{R}$ where $\mathbf{R}$ may, or may not, be involutory. If the eigen-vectors of $\mathbf{R}$ be (r_{01}, r_{11}) and (r_{02}, r_{12}) then a necessary and sufficient condition that $\mathbf{AB} \ldots \mathbf{JK}$ be an involutory matrix is

$$\begin{vmatrix} r_{01}^2 & r_{01}r_{11} & r_{11}^2 \\ r_{02}^2 & r_{02}r_{12} & r_{12}^2 \\ k_0 & k_1 & k_2 \end{vmatrix} = 0,$$

where

$$\mathbf{K} = \begin{pmatrix} k_1 & -k_0 \\ k_2 & -k_1 \end{pmatrix}$$

[An eigen-vector of an n by n matrix $\mathbf{A}$ is a non-zero vector $\mathbf{x}$ satisfying $\mathbf{Ax} = \lambda \mathbf{x}$ for an appropriate scalar λ. There are, in general, n independent eigen-vectors corresponding to the n values of λ given by $| \lambda \mathbf{I} - \mathbf{A} | = 0.$]

Theorem 3, Corollary 3, gives

Theorem 7. If $\mathbf{A}_1, \ldots, \mathbf{A}_n$ be an odd number of involutory 2 by 2 matrices, where

$$\mathbf{A}_i = \begin{pmatrix} a_{1i} & -a_{0i} \\ a_{2i} & -a_{1i} \end{pmatrix},$$

then the relations

$$\begin{Vmatrix} a_{01} & a_{02} & \ldots & a_{0n} \\ a_{11} & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} & \ldots & a_{2n} \end{Vmatrix} = 0$$

imply that the product $\mathbf{A}_1 \mathbf{A}_2 \ldots \mathbf{A}_n$ is an involutory matrix.

Corollary. If $\mathbf{A}$ and $\mathbf{B}$ are involutory then so are $(\mathbf{AB})^n\mathbf{A}$ and $(\mathbf{AB})^n\mathbf{B}$. This is also obvious algebraically and holds for square matrices of any order.

Relation to Orthogonal Matrices.

We now consider the relation of the above results to orthogonal matrices of order three. In the remainder of this paper all matrices denoted by capital letters are square matrices of the third order, all vectors are denoted by lower case letters and are regarded as 3 by 1 matrices, and the transpose of a matrix will be signified by a dash. For any vector such as $\mathbf{a}$ we shall assume that $\mathbf{a}' = (a_1, a_2, a_3)$. Also, a point P of coordinates (p_1, p_2, p_3) shall be referred to as the point $\mathbf{p}$ or the point of coordinate vector $\mathbf{p}$ (i.e. using the corresponding lower case symbol).

If the conic s, used above, be taken in the plane π at infinity $(x_0 = 0)$ with equation

$$x_1^2 + x_2^2 + x_3^2 = 0,$$

then any (non-singular) collineation of the plane π into itself which leaves s invariant is an orthogonal transformation ; and the converse is true. Writing this collineation as

$$\rho \mathbf{x}^* = \mathbf{A} \mathbf{x}$$

then $\mathbf{A}$ may be taken as an orthogonal matrix. If $\mathbf{A}$ is real with determinant equal to $+1$ then this transformation corresponds to a proper rotation in ordinary cartesian space.

In the geometrical results above we were concerned exclusively with transformations of the points on the conic s. It is clear that any projectivity on s can be extended into a collineation of the whole plane π and, moreover, this extension is unique. For, if T and T^* are two such extensions then $T^{-1}T^*$ would leave every point of the non-degenerate conic s invariant. On examining the possible types of collineations in a plane corresponding to the six distinct Segre characteristics, [Todd, 1947] it follows that $T^{-1}T^*$ must be the identity ; that is, $T=T^*$.

In particular the involution P on s corresponding to the point P extends (uniquely) into an involutory collineation of π, namely, the harmonic inversion in the point P and its polar p with respect to s. We shall refer to this as the involutory collineation P determined by the point P. This can be interpreted in ordinary cartesian space as a reflection of (unsensed) lines through the origin O in a plane through O.

The matrix of the involutory collineation P is easily found as follows. The polar of the point P, of coordinate vector $\mathbf{p}$, with respect to the conic $\mathbf{x}'A\mathbf{x}$, is $\mathbf{p}'A\mathbf{x}=0$. Denoting the involutory collineation determined by P by

$$\varkappa\mathbf{x}^* = P\mathbf{x},$$

we see that $\mathbf{x}$ and $\mathbf{x}^*$ must be of the form

$$\mathbf{x}=\lambda\mathbf{p}+\mathbf{q} \text{ and } \mathbf{x}^*=-\lambda\mathbf{p}+\mathbf{q}$$

where $\mathbf{q}$ is the point of intersection of the polar of P with the line joining P to $\mathbf{x}$. Therefore

$$\mathbf{x}^*=\mathbf{x}-2\lambda\mathbf{p}.$$

Since Q lies on the polar of P

$$\mathbf{p}'A(\mathbf{x}-\lambda\mathbf{p})=0,$$

giving

$$\lambda=(\mathbf{p}'A\mathbf{x})/\mathbf{p}'A\mathbf{p}.$$

Hence

$$\varkappa\mathbf{x}^*=\left(I-\frac{2\mathbf{p}\mathbf{p}'A}{\mathbf{p}'A\mathbf{p}}\right)\mathbf{x},$$

and so P may be taken in the form

$$P=\rho\left(I-\frac{2\mathbf{p}\mathbf{p}'A}{\mathbf{p}'A\mathbf{p}}\right).$$

Now the coordinate vectors of points not on s may be normalised to unit magnitude and the conic s may be taken as $\mathbf{x}'\mathbf{x}=0$. Then $A=I$, $\mathbf{p}'\mathbf{p}=1$ and we have P in the form (taking $\rho=-1$ to make $|P|=1$),

$$P=-I+2\mathbf{p}\mathbf{p}'. \tag{3}$$

P is symmetric, orthogonal and involutory (any two of these adjectives imply the third). Moreover, it is clear that every symmetric proper orthogonal matrix of the third order must be expressible in the form (3).

Theorem 1, Corollary 1, therefore yields

Theorem 8. The product of two symmetric orthogonal matrices P, Q is also symmetric and orthogonal if, and only if, $\mathbf{p}'\mathbf{q}=0$.

Interpreted in ordinary cartesian space this may be stated as follows :

The product of two reflections, in planes α, β, is a reflection if, and only if, α is perpendicular to β. (The reflections are of unsensed lines through the origin O in planes through O.)

Theorem 2 and its corollary also give

Theorem 9.   The product of three symmetric orthogonal matrices **A, B, C** is also symmetric and orthogonal if, and only if, the scalar triple product [**a, b, c**] vanishes.   (It is assumed that each of the three matrices is expressed in the form (3) above.)

In ordinary cartesian space this can be stated as follows :

The product of three reflections **A, B, C**, in planes α, β, γ, respectively, is a reflection if, and only if, α, β, γ have a line in common.

Suppose this condition is satisfied and the product is a reflection **D**.   In the plane π, the points A, B, C, D will lie on a line meeting s in U, V such that (U, V), (A, C), (B, D) are in involution.   Therefore

$$(UV, AB) = (VU, CD) = (UV, DC).$$

But $(UV, AB) = e^{2i\theta}$ where θ is the angle between the planes α and β. [See e.g. Baker, 1928, whose terminology we follow here.]   That is, if β is obtained from α by rotation through an angle θ then δ is obtained from γ by rotation through $-\theta$.

Rotations.   Any (non-singular) collineation **R** of the plane π which leaves s invariant induces a projectivity on s whose self-corresponding points are, say, U, V.   Let us denote the line UV by l and the pole of l with respect to s by L. Since U and V are self-corresponding points of **R**, it follows that l is a self-corresponding line on which **R** induces a projectivity with U, V as the united points.   The characteristic cross ratio of this projectivity is (UV, PP') where P is on l and $P' = \mathbf{R}P$, and this cross ratio is independent of the choice of P on l. In cartesian space with origin O, the angle POP' $(=\theta$, say) is given by

$$2i\theta = log\ (UV, PP'),$$

and OL is normal to the plane Ol.   It is therefore clear that the collineation **R** corresponds, in cartesian space, to a rotation about the vector l as axis through an angle θ.

The lemma A preceding Theorem 3 yields

Theorem 10.   Any orthogonal matrix can be factorised into the product of two symmetric orthogonal matrices, each of the form $-\mathbf{I} + 2\mathbf{pp}'$, and this can be done in ∞^1 ways.

In ordinary cartesian space, we may say, with more detail :

Any rotation **L**, about an axis l through an angle φ, can be expressed as the product **MN** of two reflections, in planes μ, ν, respectively, say ; μ must be taken arbitrarily through l and ν is then uniquely determined.   (Or, ν could be chosen arbitrarily and then μ is uniquely determined.)

We will show further, now, that the angle between μ and ν is $\frac{1}{2}\varphi$.

Using the notation of Lemma A, let PN meet s in S and SQ meet UV in H. Therefore

$$\mathbf{L} = \mathbf{MN} = \mathbf{NH}.$$

Now the pencil of conics through the points P, Q, R, S determine an involution on l in which (M, N), (U, V) are pairs and N is a double point ; the other double point is G, the intersection of l with the polar of N.   Therefore

$$\mathbf{ML} = \mathbf{MMN} = \mathbf{MN} = H.$$

As M varies on l, the points M, N are in $1-1$ correspondence in which U, V are the united points ; also $M \rightarrow N$ and $N \rightarrow H$.   So

$$(UV, MN) = (UV, NH)$$

and hence

$$(UV, MH) = (UV, MN)^2.$$

It follows that the angle from μ to ν is $\frac{1}{2}\varphi$.

Theorem 3 now gives

Theorem 11. The product ˙of reflections A, B, . . ., J, K (in planes α, β, . . ., ϰ, say) is also a reflection if, and only if, the plane ϰ passes through the axis of the rotation defined by AB . . . J.

It should be noticed that this statement remains valid when AB . . . J is a reflection if we call the normal to the plane defining the reflection its " axis ".

A purely algebraic formulation of this result may be conveniently given in terms of real matrices. A real orthogonal matrix R, if it is not symmetric, has one, and only one, real eigen vector which we shall denote by the corresponding lower case letter r. Let A, B, . . ., J, K be a set of real, symmetric, orthogonal (and, therefore, also involutory) matrices ; and also let AB . . . J = R where R is not symmetric. Then a necessary and sufficient condition that AB . . . JK be symmetric is r'k = 0. If R is symmetric, but is not the identity, the above condition is still valid provided r is taken to be that eigen vector of R which is uniquely determined, i.e. r is the normal to the plane defining the reflection R. The case R = I is trivial.

Vector Form for Rotations. The above results enable us to obtain vector forms for a rotation and for the composition of two rotations, the axis of a rotation being specified by a unit vector and the angle by a scalar.

Every real, proper, orthogonal matrix A is of the form e^Q where Q is skew-symmetric [Taber, 1892]. Suppose

$$Q = \begin{pmatrix} 0 & -q_3 & q_2 \\ q_3 & 0 & -q_1 \\ -q_2 & q_1 & 0 \end{pmatrix},$$

where the q_i are real numbers, not all zero. The characteristic equation of Q is

$$\lambda^3 + (q_1{}^2 + q_2{}^2 + q_3{}^2)\lambda = 0,$$

so that we have, by the Hamilton-Cayley theorem,

$$Q^3 = -q^2 Q,$$

where $q' = (q_1, q_2, q_3)$ and $q = |q|$.

Writing $Q = qS$, then

$$S = \begin{pmatrix} 0 & -s_3 & s_2 \\ s_3 & 0 & -s_1 \\ -s_2 & s_1 & 0 \end{pmatrix},$$

where $s_i = q_i/q$; thus the vector defined by $s' = (s_1, s_2, s_3)$ is a unit vector. We now have $S^3 = -S$ and therefore

$$A = e^Q = e^{qS}$$

$$= I + qS + \frac{q^2 S^2}{2!} - \frac{q^3 S}{3!} - \frac{q^3 S^2}{4!} + \ldots$$

$$= I + \sin q S + (1 - \cos q) S^2 \qquad (4)$$

Now $Ss = s \times s = O$ and therefore $S^2 s = O$.

Hence $As = s$ and it follows that s is the axis of the rotation A defined by A.

Let the angle of rotation of A be θ, so that A is fully and uniquely determined by s and θ. Regarding s, and therefore S, as fixed, we may write

$$f(\theta) = A = e^{qS} = I + \sin q S + (1 - \cos q) S^2 \qquad (5)$$

where q is some function of θ. For any integer n we have

$$f(n\theta) = A^n = e^{nqS} = I + \sin nq S + (1 - \cos nq) S^2, \qquad (6)$$

and, in fact, this holds for any rational number n. It can now be readily shown that $q = 0$ (mod 2π). Therefore, the rotation has matrix

$$\mathbf{A} = e^{\theta \mathbf{S}} = \mathbf{I} + \sin\ \theta \mathbf{S} + (1 - \cos\ \theta)\mathbf{S}^2,$$

and hence, for any vector $\mathbf{x}$,

$$\mathbf{Ax} = A\mathbf{x} = \mathbf{x} + \sin\ \theta \mathbf{s} \times \mathbf{x} + (1 - \cos\ \theta)\mathbf{s} \times (\mathbf{s} \times \mathbf{x}), \qquad (7)$$

since $\mathbf{Sx} = \mathbf{s} \times \mathbf{x}$ and $\mathbf{S}^2\mathbf{x} = \mathbf{S}(\mathbf{Sx}) = \mathbf{s} \times (\mathbf{s} \times \mathbf{x})$.

Now let $\mathbf{A}$, $\mathbf{B}$ be two rotations about axes $\mathbf{a}$, $\mathbf{b}$ (unit vectors) through angles 2θ, 2φ, respectively. In the plane at infinity, let A, B be the points of coordinate vectors $\mathbf{a}$, $\mathbf{b}$, and let their polars, with respect to s, be λ, μ, respectively; also denote the point (λ, μ) by N; N is therefore the pole of AB and we may take $\sin \gamma\ \mathbf{n} = \mathbf{a} \times \mathbf{b}$. By Theorem 10, there exists a point M on λ and a point L on μ such that

$$\mathbf{A} = \mathbf{MN} \text{ and } \mathbf{B} = \mathbf{NL}.$$

Hence $\mathbf{AB} = \mathbf{ML}$. Denoting the pole of ML by C (given by a unit vector $\mathbf{c}$) and the interval ML by ψ we see that $\mathbf{AB}$ is a rotation $\mathbf{C}$ about the axis $\mathbf{c}$ through the angle 2ψ. It follows from Theorem 10 that $M \rightarrow N$ by a rotation about a through angle θ, and so we have, using (7),

$$\mathbf{m} = \mathbf{n} - \sin\ \theta \mathbf{a} \times \mathbf{n} + (1 - \cos\ \theta)\mathbf{a} \times (\mathbf{a} \times \mathbf{n}).$$
$$= \cos\ \theta \mathbf{n} - \sin\ \theta \mathbf{a} \times \mathbf{n}.$$

Similarly,

$$\mathbf{l} = \cos\ \varphi \mathbf{n} + \sin\ \varphi \mathbf{b} \times \mathbf{n}.$$

Therefore $\cos\ \psi = \mathbf{l}.\mathbf{m} = \cos\ \theta\ \cos\ \varphi - \sin\ \theta\ \sin\ \varphi\ (\mathbf{a} \times \mathbf{n}).(\mathbf{b} \times \mathbf{n})$
$$= \cos\ \theta\ \cos\ \varphi - \sin\ \theta\ \sin\ \varphi\ \cos\ \gamma.$$

where $\cos\ \gamma = \mathbf{a}.\mathbf{b}$, and so we have obtained an expression for the angle 2ψ of the resultant rotation $\mathbf{C}$.

To find the axis of $\mathbf{C}$ we have

$$\mathbf{m} \times \mathbf{l} = (\sin\ \theta\ \cos\ \varphi)\mathbf{a} + (\cos\ \theta\ \sin\ \varphi)\mathbf{b} - \sin\ \theta\ \sin\ \varphi\ (\mathbf{a} \times \mathbf{n}) \times (\mathbf{b} \times \mathbf{n})$$
$$= (\sin\ \theta\ \cos\ \varphi)\mathbf{a} + (\cos\ \theta\ \sin\ \varphi)\mathbf{b} - (\sin\ \theta\ \sin\ \varphi)\mathbf{a} \times \mathbf{b}.$$

The axis $\mathbf{c}$ of $\mathbf{C}$ is parallel to $\mathbf{m} \times \mathbf{l}$ and is therefore determined.

If we write $\mathbf{a}_1 = \tan\ \theta \mathbf{a}$, $\mathbf{b}_1 = \tan\ \varphi \mathbf{b}$ then $\mathbf{c}$ is parallel to the vector $\mathbf{a}_1 + \mathbf{b}_1 - \mathbf{a}_1 \times \mathbf{b}_1$.

ACKNOWLEDGEMENTS.

REFERENCES.

Baker, H. F., 1930. Principles of Geometry, 2, 167 *et seq.*
Salmon, G., 1850. Treatise on Conic Sections, p. 282.
Taber, H., 1892. *Proc. Amer. Acad. Arts Sc.*, 27, 163.
Todd, J. A., 1947. Projective and Analytical Geometry, p. 168, §5.5.

NATURE AND OCCURRENCE OF PEAT AT HAZELBROOK, NEW SOUTH WALES.

By J. A. Dulhunty, D.Sc.

Occurrence and Origin.

Small lenses of well-preserved peat occur at depths of 5 to 6 feet in sandy soil about one mile north-west of Hazelbrook in the Blue Mountains. The material is of considerable interest owing to its unusual mode of occurrence and origin, and its significance in relation to early stages of coalification.

High-humus soils are common on elevated country, between 2000 and 4000 feet above sea level in the Eastern Highlands of New South Wales, but true peat has not formed as climatic conditions were not suitable during late Tertiary and Pleistocene time. In the Southern Highlands of New South Wales peat is accumulating at isolated places above 6000 feet on the Kosciusko Plateau, but alpine conditions in that area are quite different from those in any other part of New South Wales. In view of this, the occurrence of true peat at Hazelbrook (1000 feet above sea level) was investigated with the object of explaining its presence where climatic conditions have not been suitable for normal peat-formation.

The peat occurs as irregular lenses, up to 1 inch in thickness and 3 feet in diameter, distributed sporadically at the base of about 6 feet of sandy soil which lies on soft, partly weathered Hawkesbury Sandstone (Triassic) in a relatively mature valley of late Tertiary or early Pleistocene age. The sandy soil becomes more compact as it passes downwards from the surface. It also contains pebbly layers and horizons of ferruginous concretions which are typical of the underlying and surrounding beds of Triassic sandstone. The sandstone contains an argillaceous cement and relatively deep weathering or softening is common on old surfaces from which sand and clay have not been washed away. The pebbly layers and horizons of ferruginous concretions, in the sandy soil above the peat, lie parallel to the bedding of the underlying sandstone rather than the surface. This strongly suggests that the soil represents weathered or softened sandstone rather than recently transported alluvium.

From the nature of occurrence, outlined above, it appears evident that the peat is embedded in weathered Triassic sandstone, which presents an unusual problem as the peat has suffered very little compression and, from its general nature and properties, it is certainly much younger than the sandstone. At all other places plant material embedded in the Hawkesbury Sandstone during deposition is now in the form of hard bright coal of bituminous rank.

A possible explanation of the origin of the peat is suggested by the behaviour of roots of contemporary plants growing in the sandy soil above the peat. The partly weathered sandstone immediately beneath the peat appears to be a harder bed which has resisted weathering more than the overlying material. Roots of contemporary plants have found their way down through the completely softened sandstone and some have penetrated the peat lenses, but they have not entered the partly weathered sandstone underlying the peat. This suggests that the peat may have been formed by roots penetrating to the partly weathered

sandstone bed and spreading out to form " root mats " over a long period of time.   Root material first introduced into the weathered sandstone in this way could have been preserved as a result of anaerobic conditions prevailing beneath ground-water level.   With time, more roots probably entered the small root mats to become preserved after death, and thus add to the bulk of organic material in the peat lenses.   Such a process would explain the occurrence of Pleistocene peat in weathered Triassic sandstone, and also the preservation of plant material to form peat in an area where climatic conditions have not been suitable for preservation at the surface in the normal manner.

The mode of origin outlined above was suggested after geological examination of the occurrence, and it was evident that if the peat had been formed in that way it would not contain pollen, spores or those parts of plants which extend above the surface of the ground.   If, however, it had been deposited at the surface and subsequently buried it would be certain to contain aerial plant remains. In view of this, samples of the peat were submitted to Mr. J. Waterhouse, Department of Botany, University of Sydney, for microscopical examination with the object of obtaining further evidence relating to the nature of the material and its origin.   His conclusions were as follows :

" Macroscopically, there appear to be roots in various stages of disintegration ramifying throughout the material.   It was difficult to section the peat for microscopic study as it did not respond favourably to the usual procedure of wax-embedding.   However, sections which were obtained exhibited normal root structures and revealed among the débris bodies that appear to be vesicles and subtending hyphæ of vesicular-arbuscular mycorrhizal fungi which normally occur associated with roots of some plants.   No pollen grains were observed. The examination would therefore suggest that the peat has not originated from surface material, but rather that it was formed by accumulation of root material."

The foregoing results support conclusions based on geological evidence that the peat represents an accumulation of root material at some depth beneath the surface where it was preserved under anaerobic conditions below ground-water level.   It follows that the occurrence does not necessarily indicate the recent existence of climatic conditions normally required for the formation of peat.

NATURE AND PROPERTIES.

The peat consists of soft fibrous root fragments, up to 8 inches in length and about $\frac{1}{4}$ inch in diameter, set in a matrix of finely divided root material and a stiff structureless gel-like substance.   As a whole the peat is firm and compact but can be easily cut with a knife, and it is of a somewhat springy or rubbery nature when pressed or bent by hand.   When taken from the moist sandy soil in which it occurs, the peat can be preserved in its original condition by storing in a closed jar.   It also retains its original condition if placed over water in a closed jar, but when actually immersed it takes up, or absorbs, large amounts of water and swells to several times its original volume.   When air-dried, the peat shrinks to about one-half its volume and becomes hard and brittle, but if immersed in water it readily takes up moisture and returns to its original condition.   This property indicates that it has not reached the state of maturity, with respect to development of colloidal or micelle structure, at which irreversible physical changes occur when water is removed by drying (Dulhunty, 1946 and 1949).

For the purpose of chemical analysis and determination of maximum inherent moisture the peat was separated by hand into three components : A, Large pieces of root material.   B, That portion of the peat which consisted mainly of finely divided fibrous material and a small amount of gel-like substance. C, The gel-like substance with very little fibrous material: Ultimate and proximate analyses were carried out on the three components, and values for

maximum inherent moisture were determined by Controlled Vaporisation of Adherent Moisture (for details of process see Dulhunty, 1947). Results of analyses and moisture values, shown in Table I, indicate that components A and B are very similar with respect to carbon, hydrogen and moisture, but ash and volatiles are considerably lower in A. Component C is lower in carbon but somewhat higher in hydrogen and moisture than components A and B.

TABLE I.

Analytical Data and Moisture Properties of Components in Hazelbrook Peat.

Peat Component.	Percentage Ash-free Dry Peat.				Percentage Dry Peat.	
	Carbon.	Hydrogen.	Vols.	Fixed Carbon.	Maximum Inherent Moisture.	Ash.
A	53·10	5·22	66·7	33·3	40·31	2·74
B	54·08	5·62	78·1	21·9	40·12	8·90
C	47·3	5·88	76·1	23·9	56·00	6·80

Component A, large pieces of root material, would appear to be the precursor of vitrain in higher rank coal, whilst component B, consisting of more finely divided fibrous material together with some of the gel-like substance, would probably become a canneloid clarain if coalification were to continue to bituminous rank. The low carbon content and high moisture value of the structureless gel-like substance, component C, suggest that it is some form of humic degradation product derived by limited biological decay of the root material. This substance probably represents the peat-stage or precursor of a homogeneous structureless cannel-coal constituent with unusually low hydrogen content and volatile yield owing to the complete absence of spores, cuticle and resin, which normally characterise cannel derived from surface plant-material.

The carbon contents and volatile yields of components A and B indicate that the peat is very immature with respect to chemical rank as changes have advanced only a little beyond the average composition of wood which contains about 50% carbon and yields about 80% volatiles. The small change which has taken place is evidently associated with the biological processes of preliminary decay followed by preservation under more or less anaerobic conditions.

Relationships between maximum inherent moisture and rank or carbon content, for vitrains of all rank from peat to anthracite, were recently investigated (Dulhunty, 1948). It was shown that in the peat stage the woody precursors of vitrain, with 55% to 60% carbon, have moisture values of 30% to 50%. As rank increases moisture rises to between 70% and 120% at brown-coal rank (carbon about 70%), where it reaches a maximum in the carbon-moisture relationship. With further increase in rank, moisture then falls to less than 5% at the well-known minimum at high-rank bituminous stage. In the case of the woody constituents, components A and B, in the Hazelbrook peat, the moisture values of about 40% for 53% to 54% carbon are in keeping with the general relationship established for the woody constituents of peats formed in the normal manner. The relatively low moisture values of about 40% indicate that the woody constituents of the Hazelbrook peat are very immature with respect to physical rank as well as chemical rank, and it is probable that much of the original physical structure of cellulose and lignin still remains, and that only a

limited amount of the true gel, or colloidal structure, of higher-rank peats and brown coals has developed. The somewhat higher moisture value of 56% for the gel-like substance, with 47·3% carbon suggests that its physical rank is in advance of its chemical rank, and that practically all the original ultra-fine structures of the plant materials have been replaced by the colloidal structures which represent the first stages in the formation of the micelle structures in higher-rank coals. This accounts for the springy or rubbery nature of the peat.

When carbon content reaches about 60%, and maximum inherent moisture rises to between 60% and 70%, low-rank coals reach the stage at which irreversible physical changes occur on drying (Dulhunty, 1948). At this stage it is believed that the ultra-fine structure consists essentially of well-developed micelles, the majority of which are just touching with very small contact points. The Hazelbrook peat has not yet attained this rank-stage, with respect to either physical or chemical rank. It is probable that its ultra-fine structure, in addition to residues of the original cellulose and lignin structure, consists mainly of " primary units " (Bangham, 1943), which eventually segregate to form micelles, dispersed in a watery medium. This degree of colloidal development, with the absence of micelles touching at contact points, would explain the fact that the peat can be dried and resaturated without causing permanent change in its ultra-fine structure. Also the condition of component C, which appears to consist almost entirely of unsegregated primary units dispersed in a watery medium, would account for the fact that the peat takes up water and swells to several times its original volume if immersed after removal from its place of occurrence where it is confined under slight pressure from the weight of overlying sand.

In general, it appears that the Hazelbrook material is a true but immature peat in which plant constituents have been partly changed to humic products representing the first step in the building of the complex " coal molecule ", and that the material is in the earliest stages of the process of physical development which eventually gives rise to the well-organised micelle structure of coal. It is believed that further study of the physical and organic chemistry of such peats may provide important data and contribute towards a better understanding of the mechanism by means of which plant material is changed to coal.

REFERENCES.

Dulhunty, J. A., 1946. Physical Changes Accompanying Drying of Some Australian Lignites. THIS JOURNAL, 80, 82.

——————— 1947. Determination of Maximum Inherent Moisture in Coal by Controlled Vaporisation of Adherent Moisture. THIS JOURNAL, 81, 60.

——————— 1948. Relation of Rank to Moisture of Vitrain, and Permanent Physical Changes on Drying. THIS JOURNAL, 82, 286.

Bangham, D. H., 1943. Proc. Conference on Ultra-fine Structure of Coals and Cokes. Brit. Coal Util. Res. Ass. H. K. Lewis and Co. Ltd., London, p. 18.

THE RESOLUTION OF THE TRIS o-PHENANTHROLINE NICKEL II ION.

By F. P. DWYER, D.Sc.,

and (MISS) E. C. GYARFAS, M.Sc.

When excess of o-phenanthroline is added to a nickel salt solution, pink coloured compounds result which have been shown to have the constitution $Ni(phenan)_3X_2.nH_2O$ (Pfeiffer and Tappermann, 1933). These substances are analogous to the tris $2:2'$ dipyridyl compounds $Ni(dipy)_3X_2.nH_2O$ which are also pink and have been resolved into enantiomorphous forms (Morgan and Burstall, 1931). With two molecules of phenanthroline to one of nickel salt, blue compounds may be isolated (Pfeiffer and Tappermann, *loc. cit.*), of the composition $Ni(phenan)_2X_2.nH_2O$. Whether these compounds are the octahedral complexes $[Ni(phenan)_22H_2O]X_2.(n-2)H_2O$ or simply hydrated 4-covalent complexes is unknown, but analogy with the hexammine and tetrammine series of nickel compounds supports the latter interpretation.

In the present communication the resolution of the tris o-phenanthroline nickel ion is described and also experiments carried out in an effort to resolve the blue bis compounds. The resolution of the tris-phenanthroline nickel ion was achieved by the addition of an excess of potassium d-antimonyl tartrate to a solution of the complex chloride, when the d-tris o-phenanthroline nickel d-antimonyl tartrate separated as a highly insoluble crystalline precipitate. The optically active acid was eliminated by the addition of alkali, and the active nickel complex precipitated as the sparingly soluble perchlorate. The laevo form was obtained from the filtrate by precipitation with sodium perchlorate solution. The active perchlorates were purified by recrystallisation from warm aqueous acetone, the d,l perchlorate impurity separating as the least soluble fraction.

The optical forms were much more stable than the active forms of the tris $2:2'$ dipyridyl nickel ion. Thus, whilst Morgan and Burstall (*loc. cit.*) found that solutions of the active form of this substance racemised completely in $1\frac{1}{2}$ hours at 20° C., the phenanthroline complexes had lost only 50% of the activity in 18 hours, and at the end of $73\frac{1}{2}$ hours still possessed a slight rotation. An unexpected observation was that the racemisation rate was reduced in the presence of sulphuric acid. This effect is being studied in detail in order to gain information of the mechanism of racemisation.

Like the corresponding ruthenium compound $Ru(phenan)_3(ClO_4)_2$, whose resolution has been described previously (Dwyer and Gyarfas, 1949), when examined in the wavelengths $589\cdot0$ and $546\cdot1$ mμ, the nickel compound showed a large abnormal rotatory dispersion. The absorption and rotatory dispersion curves will be described in a subsequent communication.

When the blue solutions containing the bis-o-phenanthroline complex were treated with potassium antimonyl tartrate, pale pink precipitates of the tris phenanthroline complex were obtained even when the ratio of nickel to the base was only $1:1\cdot5$, suggesting that the bis complex was in equilibrium with the tris complex

$$3Ni(phen)_2{}^{++} \rightleftarrows 2Ni(phen)_3{}^{++} + Ni^{++}$$

This observation was confirmed by the precipitation of $Ni(phenan)_3(ClO_4)_2$ from blue solutions, which had been boiled to ensure that any of the tris compound, accidentally prepared by a local high concentration of phenanthroline during the preparation of the bis compound should be transformed. The ease of change of the bis complex to the tris obviates all possibility of resolution.

EXPERIMENTAL.

A 4 dm. tube was used for all measurements of rotation.

d-Tris o-Phenanthroline Nickel d Antimonyl Tartrate.

d,l Tris o-phenanthroline nickel chloride was prepared as described by Pfeiffer and Tappermann (*loc. cit.*), by the addition of finely divided o-phenanthroline monohydrate (3·0 g.) to a solution of nickel chloride hexahydrate (1·2 g.) in water (100 mls.). The mixture was stirred until the phenanthroline had dissolved completely, and to the resulting red solution was added slowly a solution of potassium antimonyl tartrate (4·8 g.—3 mols.) in water (30 mls.). On scratching the sides of the vessel, a pink crystalline precipitate was obtained. The solution was cooled rapidly from room temperature to approximately 5° C. in ice and filtered. The precipitate was washed with ice water and purified by solution in 0·1 N caustic soda (50 mls.) and after filtration, precipitated by the addition of acetic acid and a little potassium antimonyl tartrate. The pure substance crystallised in pale pink needles.

A 0·02% solution in N/100 sodium hydroxide gave $\alpha = +0 \cdot 76°$; whence $[\alpha]_D^{15} = +950°$.

Found : N = 6·45% ; Sb = 18·79%.

Calculated for $[Ni(C_{12}H_8N_2)_3].[SbO.C_4H_4O_6].2.7H_2O$: N = 6·49% ; Sb = 18·79%.

d,l-Tris o-Phenanthroline Nickel Perchlorate Dihydrate.

The inactive perchlorate prepared by the addition of sodium perchlorate solution to a solution of the inactive chloride gave pink rectangular prisms from hot aqueous acetone. The compound was very sparingly soluble in water.

Found : Ni = 7·040%.

Calculated for $[Ni(CH_8N_2)_3](ClO_4)_2.2H_2O$: Ni = 7·036%.

d-Tris o-Phenanthroline Nickel Perchlorate Trihydrate.

The d tris o-phenanthroline nickel d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 mls.) by shaking at room temperature and the solution filtered. Sodium perchlorate solution was then added drop by drop, with scratching of the sides of the vessel when the d- perchlorate precipitated in pale pink micro crystals. After washing with ice water, the precipitate was dissolved in warm 30% acetone in water, and fractionally precipitated with sodium perchlorate. The first fraction was discarded and the more soluble fractions combined and recrystallised from aqueous acetone by the addition of sodium perchlorate. The substance crystallised in flat pink plates and was appreciably soluble in cold water to give a pink solution. A 0·02% solution in water gave $\alpha_D = +1 \cdot 17°$ and $\alpha_{5461} = +1 \cdot 39°$, whence $[\alpha]_D^{15} = +1463°$ and $[\alpha]_{5461}^{15} = +1738°$; or $[M]_D^{15} = +12,470°$ and $[M]_{5461}^{15} = +14,810°$.

Found : Ni = 6·85% ; N = 9·25%.

Calculated for $[Ni(C_{12}H_8N_2)_3](ClO_4)_2.3H_2O$: Ni = 6·89% ; N = 9·23%.

l-Tris o-Phenanthroline Nickel Perchlorate Trihydrate.

The residual solution after the precipitation with potassium antimonyl tartrate was strongly laevo rotatory and was treated carefully with sodium perchlorate solution, avoiding an excess to prevent the precipitation of potassium perchlorate. Alternatively it was treated with sodium iodide solution and the insoluble iodide dissolved in aqueous acetone and then precipitated as the perchlorate. The perchlorate precipitate was recrystallised as for the d form above, and gave flat pink plates of the pure laevo perchlorate. Occasionally this substance appeared in a yellow

dimorphous form if the aqueous acetone solution was too hot.   The yellow form gave a pink solution in water and had the same rotation as the pink form.

A $0 \cdot 02\%$ solution in water gave $\alpha_D = -1 \cdot 17°$ and $\alpha_{5461} = -1 \cdot 39°$, whence $[\alpha]_D^{15} = -1463°$ and $[\alpha]_{5461}^{15} = -1738°$;   or $[M]_D^{15} = -12{,}470°$ and $[M]_{5461}^{15} = -14{,}810°$.

Found : Ni = $6 \cdot 89\%$; N = $9 \cdot 21\%$.

Calculated for $[Ni(C_{12}H_8N_2)_3](ClO_4)_2.3H_2O$: Ni = $6 \cdot 89\%$; N = $9 \cdot 23\%$.

SUMMARY.

Tris o-phenanthroline nickel perchlorate has been resolved through the antimonyl tartrate.   The optical forms were much more stable then those of the tris 2 : 2′ dipyridyl nickel ion, and showed a large abnormal rotatory dispersion.

REFERENCES.

Dwyer and Gyarfas, 1949. THIS JOURNAL, **84**, 170.
Morgan and Burstall, 1931. *J. Chem. Soc.*, 2213.
Pfeiffer and Tappermann, 1933. *Zeit. f. Inorg. Chem.*, **215**, 273.

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A NOTE ON THE REACTION BETWEEN CHROMIUM II SALTS AND o-PHENANTHROLINE.

By F. P. DWYER, D.Sc.,

and H. WOOLDRIDGE, B.Sc.

Edmonds, Hammett and Chapman (1934) by the reaction between chromous acetate and o-phenanthroline obtained a red solution, which was oxidisable to a purplish red colour. The potential of the reaction, which was reversible, was found to be approximately +0·77 volt, but because of the poor colour intensity and the unsuitable colour change the substance was considered valueless as a redox indicator. The original reddish coloured solution was claimed to contain tris o-phenanthroline chromium II acetate and the oxidation reaction to be

$$Cr(phenan)_3{}^{++} \rightarrow Cr(phenan)_3{}^{+++} + e'$$

The substance responsible for the colour was not isolated and no analyses are available. The present note deals with attempts to isolate tris o-phenanthroline chromium II salts with a view to their systematic investigation and possible resolution.

Chromous acetate, or better, chromous chloride or sulphate, was found to react with phenanthroline with the production of reddish solutions, which yielded orange amorphous precipitates with chloride or sulphate ion. The filtrates from the precipitations were still coloured and gave reddish crystalline precipitates with iodides and perchlorates. The amorphous precipitates were oxidisable with ceric and dichromate to the purple coloured solutions, but the red crystalline iodides and perchlorates were not.

The orange amorphous precipitates were nearly insoluble in water and the usual organic solvents, but dissolved easily in dilute acids on warming and reprecipitated in the amorphous condition on cooling or dilution. As originally prepared, the amorphous substances contained C, H, N, S and Cr, but after purification by repeated solution in acid and reprecipitation the chromium was lost but the substances, now an orange yellow colour, were still oxidisable with potassium dichromate to a purple colour which was destroyed reversibly by reducing agents.

The red crystalline iodides and perchlorates also contained organic matter and chromium, but were not oxidisable and appeared to be impure compounds of chromium III and phenanthroline. These substances which are the chromium analogues of the ferric phenanthroline compounds, $[Fe(phenan)_2OH]_2X_4$ (Gaines, Hammett and Walden, 1936), will be described in a subsequent communication.

It thus appears that the reaction between phenanthroline and chromium II salts yields a mixture of products, and the oxidisable substance is not a chromium II compound but a reduction product of o-phenanthroline. This observation was confirmed by reducing o-phenanthroline by a variety of methods in the absence of chromium salts. The reducing agents included zinc and hydrochloric acid, zinc-amalgam and sulphuric acid, sodium amalgam, sodium in alcohol, at a mercury surface polarographically and cathodically with a lead electrode. Cathodic reduction appeared the best method of obtaining the

reduction products free from metallic impurities. The reduced solutions were orange to orange red in colour and were reversibly oxidisable. They contained at least two substances, one of which was oxidisable and the other not. One of these substances isolated as the iodide was pale yellow, non-oxidisable and had the formula $C_{12}H_9N_2.HI$. A possible structure is

This substance appears to be the first product of reduction of phenanthroline, further reduction leading to the oxidisable material which has not been isolated pure.

Preliminary experiments on the reduction of o-phenanthroline polarographically (Breyer, Buchanan and Casimir, 1948) indicate that two steps are involved, the first of one electron and the second of three.

EXPERIMENTAL.

The Reaction between Chromium II Salts and o-Phenanthroline.

Chromium III chloride hexahydrate was reduced in hydrochloric acid solution with zinc amalgam until a blue colour resulted. Solid sodium acetate was added and the red crystalline chromium II acetate was filtered in an atmosphere of carbon dioxide. The solid acetate was added directly to oxygen-free solutions of o-phenanthroline acetate, or alternatively dissolved in 0.5 N sulphuric or hydrochloric acids and added to solutions of the base in aqueous alcohol. In all experiments red solutions resulted which yielded orange precipitates with chloride, sulphate, iodide or perchlorate.

All of the precipitates were reversibly oxidisable with potassium dichromate, or permanganate, bromine water and ceric salts.

With chromous sulphate good yields of the orange substance were obtained by the subsequent addition of sodium sulphate. After washing and drying the substance gave : C=43·84% ; H=3·84% ; N=7·93% ; Cr=7·73% ; (S not estimated) ; and after solution in sulphuric acid and reprecipitation with water : C=56·06% ; H=4·98% ; N=9·50% ; Cr=2·03. With further purification the chromium was finally eliminated. The analytical figures did not agree with any possible compound, and it was concluded that the substance was an inseparable mixture.

The Cathodic Reduction of o-Phenanthroline.

The base 0.5 g. in sulphuric acid (50 cc., 1 N) was reduced at a lead cathode in a small beaker separated from the anode by the membrane of a sintered glass crucible. Current density = 0.02 amp./sq. dm. ; time = 3 hours. The solution became pale orange and was finally evaporated to half its volume. After filtration from a small amount of orange precipitate, potassium iodide was added. The reddish precipitate was crystallised from hot water, leaving a red material insoluble, and gave large translucent yellow crystals, m.p. 200–202° C. This substance was not oxidisable.

Found : C=46·23% ; H=3·38% ; N=8·63% ; I=41·0%.

Calculated for $C_{12}H_9N_2.HI$: C=46·46% ; H=3·55% ; N=9·03% ; I=40·94%.

With longer reduction the solutions became orange red, and gave precipitates with iodides and perchlorates which were oxidisable. A base could be liberated with sodium carbonate. This substance melted above 300° C., and was highly insoluble except in acids. Despite many attempts analytically pure specimens could not be isolated and the structure of the oxidisable substance is still unknown.

The Potentiometric Oxidation of the Reduction Product.

The material for these measurements was made by reduction with chromous salts or cathodically. The curves obtained, which showed only one break, were identical and within the limits of experimental error gave the same value for the redox potential.

The reaction was carried out at 0° C. to increase the stability of the oxidised product and the measurements were made as quickly as possible. The titrating agent was ceric sulphate, the electrode smooth platinum foil, and the redox potentials shown in Table I were estimated from the half titration value.

TABLE I.

Acid Concentration.	Potential. (Volts.)
H_2SO_4.	
10 N	0·90
7 N	0·88
5 N	0·87
3 N	0·86
2 N	0·86

On standing the purple colour was gradually discharged, but could be regenerated by the addition of more of the oxidising agent.

SUMMARY.

The reaction between chromium II salts and o-phenanthroline has been found to yield not complex chromium II compounds but a mixture of orange reduction products, one of which can be oxidised to a purple substance. The reduction could also be effected cathodically and by strong reducing agents such as zinc and acid. One of the reduction products isolated as the hydriodide had the formula $C_{12}H_9N_2.HI$, but was not oxidisable. The redox potential of the oxidisable material was approximately $+0·87$ volt.

ACKNOWLEDGEMENTS.

REFERENCES.

Breyer, Buchanan and Casimir, 1948. Unpublished work.
Edmonds, Hammett and Walden, 1931. *J. Am. Chem. Soc.*, **56**, 1092.
Gaines, Hammett and Walden, 1936. *Ibid.*, **58**, 1668.

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DETERMINATION OF THE BOILING POINTS OF AQUEOUS NITRIC ACID.

By L. M. SIMMONS, B.Sc., Ph.D., F.A.C.I., A.R.I.C.,
and MARTIN J. CANNY.*

With two text-figures and three tables.

Inconsistencies in the published boiling points of aqueous hydrogen chloride solutions led to the design of a static method for rapidly determining the boiling points of pure and mixed liquids which do not attack mercury, glass or tap lubricant (Simmons, 1945). The method was later developed to eliminate the tap lubricant (Simmons, 1947), and the present further adaptation described herein enables the method to be used with liquids which attack mercury, such as aqueous nitric acid.

As was the case for aqueous hydrogen chloride solutions, the boiling points of aqueous nitric acid have hitherto been determined by dynamic methods, and these are known to suffer from two important sources of error, viz. superheating and change in concentration during the distillation of all samples except the azeotropic solution. The boiling points of aqueous nitric acid given in the International Critical Tables are based on the observations of Creighton and Githens (1915) using a dynamic method due to Young (1902). Although Young claimed that with the large quantity of liquid present and the small flame that is required, there is no fear of the vapour being superheated, he later stated in his monograph (1922) that " the boiling point of a liquid can only be correctly determined by observing the temperature of the liquid itself under such conditions that ebullition is impossible ". This latter view is in accord with the conclusion arrived at by Swietoslawski (1945).

Table I shows the values published at various times for the boiling point and composition of the constant boiling mixture of water and nitric acid at or near standard pressure.

TABLE I.
Boiling Point and Composition of Constant Boiling Aqueous Nitric Acid.

Date.	Observed by.	Pressure. (Millimetres Mercury.)	B.p (° C.)	Percentage HNO₃ by Weight.	Remarks.
Before 1861	Dalton *et al.*	Not stated	120	66–70	Reported by Roscoe, 1861.
1861	Roscoe.	735	120·5	68·0	
1915	Creighton and Githens.	760	121·7– 121·8	68·18– 69·24	
1928	———	760	121·9	67·3	International Critical Tables.
1949	Simmons and Canny.	760±0·5	120·6±0·2	67·7±0·5	Present investigation.

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RESULTS.

The boiling points found for aqueous nitric acid solutions at 760 mm. by the present method are shown by curve A (Fig. 1).

That portion of curve A which represents solutions containing more than 78 per cent. by weight of HNO_3 is dotted in order to indicate that decomposition
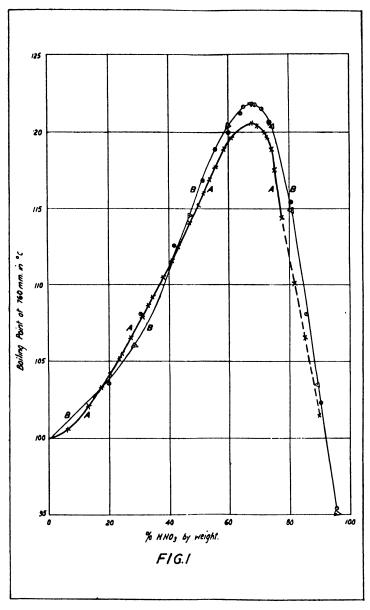
Fig. 1.—The Boiling Points of Aqueous Nitric Acid.

A. According to the present investigation, observations plotted thus : ×.

B. According to the International Critical Tables. Tabulated values plotted thus : △.

Creighton and Githens' observations plotted thus : ⊙.

takes place before the normal boiling points are reached.   In such circumstances a normal boiling point cannot strictly be quoted, for the apparent boiling point would be affected by the rate of heating, the presence of light and of catalysts, and by other factors which may affect the rate of decomposition.

The data from which curve A was plotted is given in Table II.

TABLE II.

The Boiling Points of Aqueous Nitric Acid Containing Various Percentages by Weight of HNO_3 at a Pressure of 760 mm.

Percentage HNO_3 by Weight.	B.p. (° C.)	Percentage HNO_3 by Weight.	B.p. (° C.)	Percentage HNO_3 by Weight.	B.p. (° C.)
0·0	100·0	37·9	110·5	69·2	120·4
6·1	100·6	41·0	111·7	71·7	120·0
12·9	102·1	43·0	112·5	72·2	119·7
17·0	103·3	47·3	114·1	73·7	118·9
20·3	104·2	49·7	115·2	75·3	117·6
23·3	105·2	52·0	116·0	77·4	114·4 *d.*
24·0	105·6	53·6	117·0	82·1	110·1 *d.*
27·2	106·6	56·0	117·7	85·6	106·6 *d.*
31·0	107·9	58·5	118·9	89·6	101·5 *d.*
32·7	108·7	62·0	119·6		
34·5	109·2	67·5	120·6		

d means that the sample decomposed at its boiling point.

For the purpose of comparison, Fig. 1 also shows a curve B, drawn according to the data given in the International Critical Tables.   On this curve points marked △ indicate the International Critical Tables data, while points marked ⊙ show the observations listed by Creighton and Githens.

It will be seen that the boiling point of the constant boiling mixture is listed by the International Critical Tables as more than a centigrade degree higher than that found by the present method.   It is of interest to recall that the same tables quote a maximum boiling point for hydrochloric acid more than a centigrade degree higher than that found by Simmons (1945) in confirmation of the measurements made by Bonner and Wallace (1930).
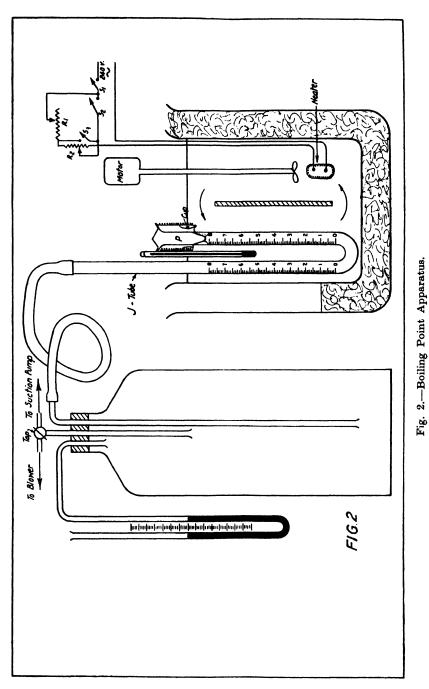
Table III is therefore submitted to replace that given on page 309 of Volume 3 of the First Edition of the International Critical Tables.

TABLE III.

B.p. (° C.) 760 mm.	B=HNO_3. M % B.
100·0	0
106·9	10
113·9	20
119·2	30
120·6	**37·2**
118·7	45
111·3	55
105·2	65
102·2	70

The last three entries in Table III refer to temperatures at which decomposition accompanies boiling.

APPARATUS AND PROCEDURE.

The J-tube shown in Fig. 2 is made of soda-glass and has an internal bore of about 7 mm. The length of the longer limb is about 20 cm.; that of the

Fig. 2.—Boiling Point Apparatus.

shorter, including the stopper P, is about 14 cm. The stopper P is ground to a good fit in the socket at the top of the shorter limb and is surrounded by a cup

to retain a liquid seal. The stopper is held in place by spring ties. Both limbs are graduated in mm. from a datum line perpendicular to the axes of the limbs near the bend to a similar line just below the socket.

The heating bath consists of a large beaker containing paraffin B.P. or other high boiling transparent liquid. The beaker is well lagged except for the top and for an observation window in the side. In the beaker is supported a glass plate which touches the sides but whose upper and lower edges are about 2 cm. respectively below the liquid surface and above the bottom of the beaker. The motor-driven propeller causes the liquid to circulate rapidly as indicated by the arrows in Fig. 2.

The heater has a resistance of about 80 ohms. Switches S_1, S_2 and S_3, and the variable resistors R_1 and R_2, enable the temperature of the bath to be raised or lowered rapidly or slowly at will.

The clean and dry J-tube, without the stopper, was clamped upright and into the shorter limb was poured enough of the nitric acid solution to reach a little more than half way up the millimetre scales. The tube was then placed in the heating bath so that the bath liquid reached about half-way up the side of the liquid seal cup when the propeller was in motion. The temperature of the bath was then rapidly raised by closing S_1 and S_2 until it was about 3° C. below the expected boiling point of the nitric acid solution. S_2 was then opened and closed judiciously until the solution had boiled gently for a few seconds in order to out-gas it. The J-tube was then removed from the bath and switches S_1 and S_2 were opened.

The rubber tube from the Winchester air bottle was then slipped over the open end of the longer limb and slight air pressure was applied by manipulating the tap until the solution in the J-tube rose to partly fill the liquid seal cup ; the meniscus in the longer limb was then near the bend in the tube. The stopper P was inserted in its socket and held in place by the spring ties. That portion of the solution which was trapped in the cup provided a liquid seal.

By this time the temperature of the bath had fallen well below the boiling point of the solution, and the J-tube was replaced in the bath, a plumb-line being used to ensure verticality of the limbs. Switches S_1 and S_3 were closed, and R_1 was adjusted so that the bath temperature rose about $\frac{1}{4}$° C. per minute ; R_1 was found to be about 170 ohms.

The barometer was then read and corrected for temperature and gravity. Using this corrected reading, the pressure in the Winchester air bottle was adjusted by manipulating the tap until the mercury manometer indicated that the total pressure in the bottle was 760 ± 0.5 mm.

A short-stem thermometer, graduated in fifths of centigrade degrees, was clamped in the bath near the closed limb so that the graduation representing the expected boiling point was visible beneath the surface of the bath liquid through the inspection window.

As the temperature neared the boiling point of the solution, a vapour bubble formed beneath the stopper, and the solution was depressed in the shorter and raised in the longer limb. S_3 was then opened and R_2 adjusted so that the temperature fell about $\frac{1}{4}$° C. per minute ; R_2 was then found to be about 50 ohms. By opening and closing S_3 the temperature was adjusted until the menisci in the two limbs were at the same level. A final adjustment of the pressure in the bottle was made to ensure that it was 760 mm., and, if necessary, the bath temperature was altered slightly to compensate for this change in pressure. When the pressure in the bottle was within $\frac{1}{2}$ mm. of 760 mm., and the levels of the solution in the two limbs differed by not more than 2 mm., the thermometer was read to the nearest 0·1° C. By manipulating S_3 the temperature was

maintained nearly constant for five minutes, after which the pressure and temperature were again adjusted as above, and the temperature was again read. The J-tube was then removed from the bath, the rubber tube removed from the longer limb, and when the tube had cooled to ambient temperature, the solution was examined to see whether any uncondensed bubbles persisted beneath the stopper.

It was found that solutions containing more than 78 per cent. by weight of HNO₃ decomposed and turned brown on heating as described above. The decomposition progressed while the temperature was maintained at a constant value, so that in order to keep the menisci of these solutions at the same level, it was necessary to increase the pressure in the air bottle. When the J-tube was subsequently cooled to room temperature, a large bubble of gas remained uncondensed beneath the stopper. The lowest concentration at which this decomposition was detected was at $77 \cdot 4\%$ HNO₃ by weight, and the decomposition became increasingly apparent at higher concentrations.

Standardization of the Thermometer. The thermometer was tested by the Standards Laboratory, Sydney, over the range 90° C. to 130° C. for total immersion to an accuracy of $\pm 0 \cdot 2°$ C., and the reported corrections were applied to the readings.

Preparation of Aqueous Solutions of Nitric Acid. Solutions containing less than $70 \cdot 2$ per cent. HNO₃ by weight were prepared by mixing weighed quantities of " Analar " concentrated nitric acid and distilled water. More concentrated solutions were prepared by mixing the " Analar " acid with a $98 \cdot 5$ per cent. nitric acid prepared as follows.

Equal volumes of " Analar " concentrated nitric acid and concentrated sulphuric acid were mixed and distilled at a pressure of about 10 cm. of mercury in an all-glass still. The resulting distillate was mixed with an equal volume of concentrated sulphuric acid and again distilled at about 10 cm. Hg.

The azeotropic solution was prepared by mixing weighed quantities of " Analar " acid and water to yield a 68 per cent. solution of HNO₃, and this was distilled at 760 mm. The first four-fifths of the distillate was rejected. The fact that the remainder of the distillate was truly the azeotropic mixture was assured by comparing its boiling point with the boiling points of mixtures of it with small quantities of concentrated acid and water respectively.

The concentrations of all solutions were determined by titration against sodium carbonate solution, using screened methyl orange indicator.

SUMMARY.

A method has been devised for the rapid determination of the boiling points of pure liquids and liquid mixtures which do not attack glass. The method obviates recourse to calculated corrections for emergent column and variations in atmospheric pressure, requires about 5 ml. of liquid, prevents sensible variations in composition of the liquid phase and avoids superheating. The method has been used to correct the list of boiling points of aqueous nitric acid appearing in the International Critical Tables. Solutions containing more than 78 per cent. HNO₃ by weight are found to decompose at or before reaching their boiling points. The constant boiling solution of nitric acid in water at 760 mm. is found to contain $67 \cdot 5 \pm 0 \cdot 5$ per cent. by weight HNO₃ and to have a boiling point of $120 \cdot 6 \pm 0 \cdot 2°$ C. at 760 mm.

REFERENCES.

Bonner, W. D., and Wallace, R. E., 1930. *J. Am. Chem. Soc.*, **52**, 1747.
Creighton, H. J. M., and Githens, F. H., 1915. *J. Franklin Inst.*, **179**, 161.
National Research Council of the U.S.A., 1928. International Critical Tables, **3**, 309. McGraw-Hill, New York.

Roscoe, H. E., 1861. *Quart. J. chem. Soc. Lond.*, 13, 146.

Simmons, L. M., 1945. THIS JOURNAL, 79, 48.

——————————— 1947. *Aust. chem. Inst. J. and Proc.*, 14, 51.

Swietoslawski, W., 1945. Ebulliometric Measurements, p. 2. Reinhold Publishing Corporation, New York.

Young, S., 1902. *J. chem. Soc.*, 81, 772.

——.———— 1922. Distillation Principles and Processes, p. 22. Macmillan, London.

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REDUCTION BY DISSOLVING METALS.

PART VIII. SOME EFFECTS OF STRUCTURE ON THE COURSE OF REDUCTIVE FISSION.

By ARTHUR J. BIRCH, M.Sc., D.Phil.

From an examination of the course of reductive fission by sodium-liquid ammonia solutions of diaryl ethers (Sowa *et al.*, 1937, 1938) and of aryl-alkyl ethers (Birch, 1947*a*) it has been concluded that the reactions proceed through transition states containing two anions: $R-O-R'+2e \rightarrow (R^-+R'-O^-)$ or (R'^-+R-O^-); the chosen transition state being the one of lower energy. By far the greater part of the energy is required to produce the carbon anions R^- or R'^-, that needed for $R-O^-$ or $R'-O^-$ being negligible by comparison (ROH, pK $\approx$ 18, is a much stronger acid than RH, pK $\approx$ 37). In practice it seems to be possible to neglect all other factors, e.g. differences in bond-strengths, and to compare the energies of the transition states on the basis of the energies of these carbon anions. The relations between structure and acidity (Birch, 1947*b*) lead to the conclusion that the greater the number of electron-repelling groups, such as alkyl, attached to a negatively charged carbon in a molecule, the greater will be its energy. Reduction should therefore proceed to give the least alkylated R-group as R^-.

This conclusion has been experimentally confirmed for aromatic systems (Birch, 1945, 1947*b*), which reduce because of resonance stabilisation of the anions, but has not been tested directly for saturated systems because they do not reduce. A confirmation of the theory in a similar case has now, however, been obtained by reducing 1 : 2-epoxypropane (I) to *iso*propyl alcohol. In this case the high ring-strain of the ethylene-oxide ring assists its reductive fission by contributing to the energy of the transition state (II). The same reduction can be carried out by sodium amalgam (Linnemann, 1866). That (II) should be formed rather than (III) can be predicted, because it contains CH_2^-, of lower energy than CH^-. The reaction cannot proceed by preliminary isomerisation to acetone, since acetone is largely unreduced under the conditions employed owing to the formation of its sodium salt.

The effect of a substituent in a benzene ring on the fission of aryl ethers (Sowa *et al.*, 1937, 1938 ; Birch, 1947*a*) is usually that to be expected from its known electronic character. The one outstanding exception so far examined is the methoxyl-group, whose influence depends on its position relative to the charged carbon atom formed in the process. In the *para*-position it shows the charge-destabilising effect to be expected from its normal electron-repelling character, but in the *ortho*-position it is charge-stabilising. In view of this unexpected dual behaviour, another reduction of a similar type, that of methoxy-phenylcarbinols, has been examined. The results confirm the orientation effects already observed : the *ortho*- and *meta*-methoxy-derivatives undergo reductive fission with loss of the hydroxyl-group, just as do the ubsubstituted carbinols (Birch, 1945), e.g. 2- and 3-methoxyphenyl-carbinol give 2- and 3-*iso*propyl-anisole, but the *para*-methoxy-derivatives preponderantly retain the hydroxyl-group and reduce instead in the benzene ring. Small amounts of the fission

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products are also obtained, but the only case where the amount is considerable is 4-methoxyphenylcarbinol (anisyl alcohol) (IV ; R, R'=H), where it is clear from work already done (Birch, 1945) that the nuclear reduced compound (V ; R, R'=H) can itself undergo reductive fission to the experimentally obtained 4-methyl-2 : 5-dihydroanisole (VI). The orientation of the two hydrogen atoms added to the benzene ring of the carbinol follows from the rule enunciated (Birch, 1944) and is confirmed by acid hydrolysis of the enol-ether group to a carbonyl. This hydrolysis is accompanied by dehydration to give the interesting diene-ketones (VII ; R, R'=H or Me).

Anisyl alcohol produces a mixture of *4-methoxy-2 : 5-dihydrophenylcarbinol* (V ; R=R'=H), hydrolysed by acid to *4-methylenecyclohex-2-enone* (VII ; R=R'=H), and 4-methyl-2 : 5-dihydroanisole (VI). 4-Methoxyphenylmethyl-carbinol (IV ; R=H, R'=Me) gives chiefly *4-methoxy-2 : 5-dihydrophenylmethyl-carbinol* (V ; R=H, R'=Me) hydrolysed to *4-ethylidenecyclohex-2-enone* (VII ; R=H, R'=Me), λ_{max} 2,850 A. Similarly, 4-methoxyphenyldimethylcarbinol (IV ; R=R'=Me) gives *4-methoxy-2 : 5-dihydrophenyldimethylcarbinol*, hydrolysed to *4-isopropylidenecyclohex-2-enone* (VII ; R=R'=Me). A particularly interesting case is the reduction of 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydro-naphthalene (VIII) to give *1-hydroxy-6-methoxy-1 : 2 : 3 : 4 : 5 : 8-hexahydro-naphthalene* (IX), hydrolysed by acid to *3-keto-1 : 2 : 3 : 5 : 6 : 7-hexahydro-naphthalene* (X). The light absorption of the last compound at λ_{max} 2,900 A. is in accord with its structure as a conjugated diene-ketone.

In all these cases, the transition state of reductive fission, e.g. (4–MeOC$_6$H$_4$CRR'–+OH$^-$) evidently requires so high an energy because of the influence of the *para*-methoxyl that the benzene ring is reduced for preference. That normal reductive fission occurs with the *meta*-methoxy compound is not astonishing, since the effect of a group in a *meta*-position is small, but the behaviour of the *ortho*-compound requires some explanation. One possible reason is that the methoxyl-group has a dual electronic character : an electron-attracting character due to the higher nuclear charge on the oxygen, and an electron-repelling character due to the unshared electrons of the oxygen atom. It is the latter which is usually more effective, especially if the group is attached to a polarisable system. There seems no reason, however, to expect one effect to operate for an *ortho*-group and the other for a *para*-group. A more likely explanation is that the *ortho*-negative charge is stabilised by cyclic hyper-conjugation, which partly transfers it to the carbon of the methoxyl-group (XI). If this explanation is correct, no stabilisation should be observed with *tert*-butyl ethers lacking the necessary hydrogen atom. It is hoped to test this experi-mentally. It may be of significance that anisoles and 2 : 5-dihydroanisoles invariably metallate in the *ortho*-position, i.e. the *ortho*-anions are the most readily formed.

The ease of reductive fission is also altered if the energy of formation of the transition state is altered in other ways. If a negative charge is placed by salt formation on the oxygen atom of an allyl or benzyl alcohol, the fission is prevented. For example, it was shown (Birch, 1945) that $PhCH=CHC(CH_3)_2OH$ is converted by sodium and alcohol in liquid ammonia into two products: $PhCH_2CH_2C(CH_3)_2OH$ by reduction of the double bond, and $PhCH_2CH=C(CH_3)_2$ by reductive fission. However, the sole product from the sodium salt $PhCH=CHC(CH_3)_2ONa$ is the dihydro-alcohol, the oxygen remaining in the molecule.

If the oxygen of an ether or alcohol is replaced by nitrogen then reductive fission of the amine is usually impossible; e.g. benzylamines, unlike benzyl ethers or alcohols, are usually unaffected by sodium in liquid ammonia. This is due to the higher energy of formation of the nitrogen anion compared with the oxygen anion : amines are very weak acids compared with alcohols. However, if the nitrogen is charged positively by quaternary salt formation it can be reductively eliminated, not as an anion, but as an electrically neutral amine. The energy of the transition state is thus greatly lowered. Although dimethylaniline gives mainly the 2 : 5-dihydro-derivative (Birch, 1946) phenyltrimethylammonium iodide gives benzene, and benzyltrimethylammonium iodide gives toluene, the nitrogen appearing as trimethylamine. The reaction is a variant of the well-known Emde reaction using sodium-amalgam (e.g. Emde and Kull, 1934), but is much more powerful. For example, the Emde method reduces phenyltrimethylammonium salts only with great difficulty (e.g. Emde, 1909). The sodium-ammonia method may prove a useful tool in alkaloid degradation (Clayson, 1949).

<center>EXPERIMENTAL.</center>

Reduction of 1 : 2-epoxypropane (I).

1 : 2-Epoxypropane (7 g.) was added to a solution of sodium (6 g.) in ammonia (200 cc.) and left until the ammonia had evaporated. The residue was cautiously decomposed with a little ice, extracted with ether (2 × 5 cc.), the solution dried with potassium carbonate, and the ether removed through a small but efficient column. The residue (3·2 g.) distilled completely at 80–82°, and gave the 3 : 5-dinitrobenzoate of *iso*propanol as cream needles m.p. 108–109°, undepressed by an authentic specimen.

Reduction of Some Methoxyphenylcarbinols.

With the exception of 4-methoxyphenylcarbinol, which was purchased, the carbinols were made by the Grignard reaction between methylmagnesium iodide and the appropriate aldehyde or ketone. The trouble reported in the literature in the preparation of 4-methoxyphenyldimethylcarbinol, due to dehydration, was not encountered if the Grignard product was worked up without the use of acid, and the ether solution well washed with water and dried over potassium carbonate.

Reduction was accomplished by dissolving the carbinol (10 g.) and ethanol (20 cc.) in ammonia (150 cc.) and adding sodium (2·2 mol.) in small pieces with mechanical stirring. In later experiments with the object of preparing the 4-methoxy-2 : 5-dihydrophenylmethyl- and dimethylcarbinol, the amount of sodium was raised to 5 mol. to ensure complete reduction of the ring. The reduction products were worked up by the addition of water (100 cc.), extraction with ether (3 × 25 cc.) and distillation. The products of reductive fission were redistilled over sodium to remove any traces of carbinol.

(a) 2-Methoxyphenylmethylcarbinol, b.p. 130°/16 mm. (Klages, 1903) gave 2-ethylanisole, b.p. 80°/14 mm. (7 g.) (found : C, 79·5 ; H, 9·0%. Calculated for $C_9H_{12}O$: C, 79·4 ; H, 8·8%.).

The product, as might be expected (Birch, 1944), contained traces of ethyldihydroanisole, because the action of 2 : 4-dinitrophenylhydrazine in 2 N hydrochloric acid and steam-distillation,

left a residue which was separated by crystallisation from alcohol into two substances. The more insoluble crystallised from ethyl acetate in dark red plates, m.p. 225°, and is probably 2-*ethylcyclohex-2-enone* 2 : *4-dinitrophenylhydrazone* (found : C, 55·0 ; H, 5·1%. $C_{14}H_{16}O_4N_4$ requires C, 55·2 ; H, 5·2%) ; the more soluble formed orange-red needles from ethanol, m.p. 118–119°, and is probably 2-*ethylcyclohex-5-enone* 2 : *4-dinitrophenylhydrazone* (found : C, 55·2 ; H, 5·0%. $C_{14}H_{16}O_4N_4$ requires C, 55·2 ; H, 5·2%) (*cf.* the reduction of 2-methylanisole, Birch, 1944).

(*b*) 2-Methoxyphenyldimethylcarbinol (Béhal and Tiffeneau, 1908) gave 2-*iso*propylanisole (7·4 g.) b.p. 93–95°/18 mm. (found : C, 79·8 ; H, 9·5%. Calculated for $C_{10}H_{14}O$: C, 80·0 ; H, 9·3%). 3-Methoxyphenyldimethylcarbinol (Béhal and Tiffeneau, 1908) reduced to 3-*iso*-propylanisole, b.p. 93–95°/16 mm. (found : C, 81·1 ; H, 9·5%. Calculated for $C_{10}H_{14}O$: C, 80·0 ; H, 9·3%). This contained a trace of the 2 : 5-dihydro-derivative, since the action of 2 : 4-dinitrophenylhydrazine as above gave 3-isopropylcyclohex-2-enone 2 : *4-dinitrophenyl-hydrazone*, bright red prisms from ethyl acetate, m.p. 155° (found : C, 54·6 ; H, 5·6%. $C_{15}H_{18}O_4N_4$ requires C, 56·6 ; H, 5·7%). With none of these compounds was there more than a trace of higher-boiling material from the reduction.

(*c*) Anisyl alcohol (with 3·0 mol. of sodium) gave a mixture of a product (A) (3·1 g.) b.p. 80°/20 mm., and (B) (4·2 g.) b.p. 135°/12 mm. Fraction (A) consisted principally of 4-methyl, 2 : 5-dihydroanisole, because the action of dilute acid (Birch, 1944) gave 4-methyl-*cyclo*hex-3-enone, semicarbazone m.p. 188°, 2 : 4-dinitrophenylhydrazone m.p. 122°. Fraction (B consisted principally of *4-methoxy-2 : 5-dihydrophenylcarbinol* (found : C, 68·9 ; H, 8·2%. $C_8H_{12}O_2$ requires C, 68·6 ; H, 8·6%) (*cf.* Birch, 1945). On warming on the steam-bath with 1 N sulphuric acid for ten minutes, it first dissolved and then an oil separated. This was taken up in ether, and distilled in a stream of nitrogen, b.p. 75–77°/12 mm. It was very unstable, and rapidly polymerised to a clear rubbery solid. It was not analysed for this reason, but gave rise to the derivatives expected for 4-methylenecyclohex-2-enone : the *semicarbazone* crystallised as cream needles from alcohol m.p. 192° (decomp.) (found : C, 57·9 ; H, 6·7%. $C_8H_{11}ON_3$ requires C, 58·2 ; H, 6·7%) (if slowly heated the derivative polymerised to a pale yellow resin without melting) ; and 2 : *4-dinitrophenylhydrazone* as large flat red needles from ethyl acetate, m.p. 160–161° (found : C, 53·8 ; H, 4·2%. $C_{13}H_{12}O_4N_4$ requires C, 54·2 ; H, 4·2%).

(*d*) 4-Methoxyphenylmethylcarbinol (Klages, 1903) reduced to give mainly *4-methoxy-2 : 5-dihydrophenylmethylcarbinol* (6·5 g.) b.p. 130°/14 mm. (found : C, 68·9 ; H, 9·3%. $C_9H_{14}O_2$ requires C, 70·1 ; H, 9·1%) hydrolysed by hot 5% sulphuric acid to *4-ethylidenecyclohex-2-enone* b.p. 100–103°/14 mm. λ_{max} 2,850, ε_{max}^{mol} 12,800 (found : C, 78·9 ; H, 8·9%. $C_8H_{10}O$ requires C, 78·7 ; H, 8·2%) ; 2 : *4-dinitrophenylhydrazone*, dark red plates from ethylacetate m.p. 164° (found : C, 55·1 ; H, 4·8%. $C_{14}H_{14}O_4N_4$ requires C, 55·6 ; H, 4·6%) ; *semicarbazone*, cream-coloured needles from ethanol m.p. 192° (found : C, 60·2 ; H, 7·5%. $C_9H_{13}ON_3$ requires C, 60·3 ; H, 7·3%).

(*e*) 4-Methoxyphenyldimethylcarbinol, b.p. 130°/14 mm. (Skraup and Freundlich, 1922) gave *4-methoxy-2 : 5-dihydrophenyldimethylcarbinol* (8 g.) b.p. 128–130°/12 mm. (found : C, 70·9 ; H, 9·0%. $C_{10}H_{16}O_2$ requires C, 71·4 ; H, 9·5%.) Acid hydrolysis gave *4-isopropylidenecyclo-hex-2-enone* (5·2 g.) b.p. 117–119°/12 mm. (found : C, 78·9 ; H, 8·7%. $C_9H_{12}O$ requires C, 79·4 ; H, 8·8%) ; 2 : *4-dinitrophenylhydrazone* m.p. 157° (found : C, 56·7 ; H, 5·1%. $C_{15}H_{16}O_4N_4$ requires C, 57·0 ; H, 5·0%) ; *semicarbazone*, cream-coloured needles from ethanol, m.p. 206–207° (found : C, 61·9 ; H, 7·8%. $C_{10}H_{15}ON_3$ requires C, 62·2 ; H, 7·8%.)

(*f*) Reduction of 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (Stork, 1947) (7 g.) was carried out by dissolving it in warm ethanol (25 cc.), and adding the solution with vigorous stirring to ammonia (250 cc.), followed by addition of sodium (7 g.) in small pieces. Working up and distillation of the product gave two fractions : (A) b.p. up to 100°/0·4 mm. (condenser in a freezing-mixture) and (B) b.p. 100–130°/0·4 mm. Fraction (A) was heated on the steam-bath with 1 N sulphuric acid for fifteen minutes, and the oil treated with aqueous-alcoholic semicarbazide acetate. The solid so obtained was the semicarbazone of 3-keto-1 : 2 : 3 : 5 :-6 : 7 : 8 : 9-octahydronaphthalene, m.p. 216°, undepressed by an authentic specimen. This is the product to be expected from 6-methoxy-1 : 2 : 3 : 4 : 5 : 8-hexahydronaphthalene. The

residual oil from the treatment was redistilled over sodium, (0·3 g.) b.p. 193–197°, and is probably a mixture of hexahydronaphthalenes (found : C, 89·2 ; H, 10·4%. Calculated for $C_{10}H_{14}$: C, 89·6 ; H, 10·4%.) Fraction (B) was redistilled, and the main fraction (3·4 g.) had b.p. 124–126°/0·4 mm. It solidified, and was crystallised from light petroleum (b.p. 40–60°) as massive prisms, m.p. 76–77° (2·9 g.). It analysed for *1-hydroxy-6-methoxy-1 : 2 : 3 : 4 : 5 : 8-hexahydronaphthalene* (found : C, 73·6 ; H, 9·0%. $C_{11}H_{16}O_2$ requires C, 73·3 ; H, 8·9%.) After refluxing with 1 N sulphuric acid for thirty minutes the pleasant-smelling *3-keto-1 : 2 : 3 : 5 : 6 : 7-hexahydronaphthalene* was distilled, b.p. 141°/12 mm. (found : C, 80·8 ; H, 8·3%. $C_{10}H_{12}O$ requires C, 81·0 ; H, 8·1%.) The light absorption λ_{max} 2,900 A, ε_{max}^{mol} 13,400, is in agreement with its formulation as a conjugated doubly-unsaturated ketone. The *semicarbazone* crystallised in cream-coloured prisms from ethanol, m.p. 210–211° (found : C, 64·4 ; H, 7·2%. $C_{11}H_{15}ON_3$ requires C, 64·4 ; H, 7·3%.)

Reduction of Quaternary Ammonium Salts.

Phenyltrimethylammonium iodide (20 g.) and alcohol (15 g.) in ammonia (100 cc.) underwent a vigorous reaction with sodium (4 g.). Addition of water (100 cc.) and separation of the oil (centrifuge) gave benzene (3 g.) b.p. 80°, $n_D^{19°}$ 1·4900, 1 : 3-dinitro-derivative m.p. 88°, undepressed by an authentic specimen. Benzyltrimethylammonium iodide similarly gave toluene, b.p. 110°, converted to 2 : 4-dinitrotoluene m.p. 70°, undepressed by an authentic specimen. Benzylamine or benzyldibutylamine under the same conditions gave no hydrocarbon product.

Reduction of 3-hydroxy-1-phenyl-3-methylbut-1-ene.

The carbinol (8 g.) was reacted in ammonia (100 cc.) with finely powdered sodium amide (2 g.) and then sodium (2 g.) added. The blue colour disappeared and was replaced by a brownish-red one. Working up by addition of water, ether extraction and distillation gave 3-hydroxy-1-phenyl-3-methylbutane (7·3 g.), b.p. 130°/18 mm. (found : C, 80·5 ; H, 9·7%. Calculated for $C_{11}H_{16}O$: C, 80·4 ; H, 9·75%.) It gave the phenylurethane m.p. 140°, undepressed by an authentic specimen.

SUMMARY.

The following reductions have been carried out by the action of sodium in liquid ammonia : 1 : 2-epoxypropane to *iso*propyl alcohol ; several 2- and 3-methoxyphenylcarbinols to the corresponding ethylanisoles, and some 4-methoxyphenylcarbinols preponderantly to 2 : 5-dihydro-derivatives, hydrolysed and dehydrated by the action of acid to 4-alkylidene*cyclo*hex-2-enones. Phenyl- and benzyltrimethylammonium iodide give benzene and toluene respectively ; the sodium salt of 3-hydroxy-1-phenyl-3-methylbut-1-ene gives solely 3-hydroxy-1-phenyl-3-methylbutane. These results are discussed in relation to the theory that such reductive fissions involve the formation of transition states containing two anions.

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REFERENCES.

Béhal, A., and Tiffeneau, M., 1908. *Bull. Soc. Chim.*, (4), 3, 315.
Birch, A. J., 1944. *J. chem. Soc.*, 432.
———————— 1945. *Ibid.*, 809.
———————— 1946. *Ibid.*, 593.
———————— 1947a. *Ibid.*, 102.
———————— 1947b. *Faraday Soc. Discussion*, 2, 246.

Clayson, D. B., 1949. *J. chem. Soc.* In the press.
Emde, H., 1909. *Arch. Pharm. Berl.*, **247**, 369.
Emde, H., and Kull, H., 1934. *Ibid.*, **272**, 469.
Klages, A., 1903. *Ber. dtsch. chem. Ges.*, **36**, 3588.
Linnemann, E., 1866. *Liebig's Ann.*, **140**, 178.
Skraup, S., and Freundlich, L., 1922. *Ber. dtsch. chem. Ges.*, **55**, 1080.
Sartoretto, P. A., and Sowa, F. J., 1937. *J. Amer. Chem. Soc.*, **59**, 603.
Kranzenfelder, A. L., Verbanc, J. J., and Sowa, F. J. *Ibid.*, **59**, 1488.
Weber, F. C., and Sowa, F. J., 1938. *Ibid.*, **60**, 94.
Stork, G. J., 1947. *J. Amer. Chem. Soc.*, **69**, 576.

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PEBBLES FROM THE UPPER HUNTER RIVER VALLEY, N.S.W.

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INTRODUCTION.

This paper presents the results of an examination of samples of pebbles from Triassic (Lower Narrabeen) conglomerates, from Permian (Upper Coal Measures, Muree Beds, Branxton Beds, Greta Coal Measures) conglomerates, and from gravels of certain river terrace soils. The samples were collected during a soil survey from a number of localities between Denman and Murrurundi (localities are given in Table 1).

The geology of the area has been described by David (1907), Browne (1924), Raggatt (1929; 1938) and Dulhunty (1939), and the physiography by Browne (1924) and Sussmilch (1940). The present Upper Hunter River and its tributaries are flowing in a wide mature valley in which they are slightly entrenched owing to uplift. The valley has a floor of Permian sediments; it is bounded on the west by an escarpment of Triassic conglomerates overlain in places by a thin bed of Jurassic sediments, and capped by Tertiary basalt; the eastern side of the valley is largely in Carboniferous rocks (Kuttung series) and Permian sediments. In Tertiary and post-Tertiary times the Hunter and its tributaries have deposited alluvial flats and river gravels. Remnants of Tertiary basalts occur in parts of the valley.

The original Upper Hunter after flowing out of the resistant Carboniferous rocks followed the strike of the soft westerly dipping Permian sediments and of the Wingen fault. The river enlarged its valley on the western side by the removal, due to sapping, of the hard resistant Triassic conglomerates overlying the Permian rocks (Browne, 1924, 139). Raggatt (1938) indicated that the original eastern boundary of Triassic deposition was not far east of Muswellbrook. If this is so, then the resistant material derived from the Triassic conglomerate would probably remain, in part at least, in the river valley, particularly near its western side. Rock wastage at the present time adds material to the valley sediments. The old valley floor remains as at least two river terraces, the higher at about 150 feet above the present river level (see 1 : 63, 360 Military Maps, sheets 368 and 377, zone 8). The river terraces often contain gravel which may (a) have been transported from different sources during river development; (b) have been derived by the weathering *in situ* of Permian conglomeratic beds; or (c) be derived wholly or in part from the Triassic conglomerates.

In order to characterise the pebbles derived from various sources, samples were collected from the localities shown in Table 1. Samples G3–G12, G14, G15, G18 were collected from locations thought to represent the 150-foot terrace level. Of the remaining samples given in Table I, G1 and G2 are representative of the Upper Coal Measure conglomerates; G16, the Muree conglomerate; G17, the Greta Coal Measure conglomerate. G13 was taken from a soil apparently developed on the Branxton Beds (details of these beds are given by Raggatt, 1929 and 1938).

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TABLE 1.
Description and Locality of Samples Examined.

Sample No.	Locality.	Description.
N1	West of Temple Court, near Murrurundi, Co. Brisbane, Pa. Murrurundi, Por. 27.	Lower Narrabeen conglomerate, top of cliff, 120 ft. above ground-level.
N2	„ „ „ „	Lower Narrabeen conglomerate, 50 ft. above ground-level.
N3	„ „ „ „	Lower Narrabeen conglomerate, 3 ft. above ground-level.
N4	South of Mt. Murella, Co. Brisbane, Pa. Tingaroo, Por. 217.	Lower Narrabeen conglomerate, base of cliffs.
N5	West of Wingen, Co. Brisbane, Pa. Wingen, Por. 168.	Lower Narrabeen conglomerate, base of cliffs.
N6	Bunnan Rd., W. of Scone, Co. Brisbane, Pa. Manbus, Por. 102.	Lower Narrabeen conglomerate, base of cliffs.
N7	„ „ „ „	Lower Narrabeen sandstone, base of cliffs.
N8	West of Dartbrook Lone, Co. Brisbane, Pa. Halscott, Por. 138.	Lower Narrabeen conglomerate, top of cliffs.
N9	„ „ „ „	Lower Narrabeen sandstone, top of cliffs.
N10	„ „ „ „	Lower Narrabeen sandstone, 80 ft. below top of cliffs.
N11	„ „ „ „	Lower Narrabeen coarse sandstone, base of Triassic outcrop.
N12	8 miles N.E. of Sandy Hollow, Co. Brisbane, Pa. Yarraman, Por. 43.	Lower Narrabeen conglomerate, base of cliffs.
N13	Denman-Merriwa Rd., Co. Brisbane, Pa. Denman, Por. 22.	Lower Narrabeen conglomerate, top of cliffs.
N14	„ „ „ „	Lower Narrabeen conglomerate, half-way up cliffs.
N15	„ „ „ „	Lower Narrabeen conglomerate, base of cliffs.
G1	S. of Muswellbrook on Hunter River, Co. Durham, Pa. Vaux, Por. 86.	Gravel from Upper Coal Measure conglomerate.
G2	S. of Kyuga, Co. Brisbane, Pa. Ellis, Por. 4.	Gravel from Upper Coal Measure conglomerate.
G3	W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 9.	Gravel from soil developed on Upper Coal Measures ; river terrace.
G4	Kingdon Ponds, Co. Brisbane, Pa. Strathearn, Por. 47.	Gravel from soil developed on Upper Coal Measures ; river terrace.
G5	W. of junction of Dart Brook and Hunter R., Co. Brisbane, Pa. Strathearn, Por. 39.	Gravel from soil developed on Upper Coal Measures conglomerate.
G6	S.W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 5.	Gravel from soil developed on Upper Coal Measures. ? River terrace.
G7	S.W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 3.	„ „ „ „
G8	Scone, Co. Brisbane, Pa. Scone, Por. 10.	Gravel from soil developed on Upper Coal Measures ; river terrace.
G9	2 miles S. Scone, Co. Brisbane, Pa. Scone, Por. 9.	Gravel from soil developed on Upper Coal Measures. ? River terrace.
G10	Near junction of Pages and Hunter R., Co. Durham, Pa. Russell, Por. 347.	„ „ „ „
G11	Hunter R., S. Muswellbrook, Co. Durham, Pa. Vaux, Por. 1.	Gravel from soil developed on Upper Coal Measures ; river terrace.
G12	Dart Brook, Co. Durham, Pa. Strathearn, Por. 35.	Gravel from soil developed on Upper Coal Measures ; probable Triassic contamination ; ? river terrace or colluvial slope.
G13	St. Helier's Brook, Co. Durham, Pa. Russell, Por. 8.	Gravel from soil developed on Branxton Beds.

TABLE 1.—*Continued.*
Description and Locality of Samples Examined.—Continued.

Sample No.	Locality.	Description.
G14	.Muswellbrook, Co. Durham, Pa. Rowan, Por. 139.	Gravel from soil developed on Branxton Beds ; river terrace.
G15	Muswellbrook, Co. Durham, Pa. Rowan, Por. 2.	Gravel from soil developed on Branxton Beds ; ? river terrace.
G16	N.E. Muswellbrook, Co. Durham, Pa. Rowan, Por. 57.	Gravel from soil developed on Muree Beds.
G17	1 mile E. Muswellbrook, Co. Durham, Pa. .Rowan, Por. 181.	Conglomerate from the Greta Coal Measures.
G18	7 miles S. Muswellbrook, Co. Durham, Pa. Vaux, Por. 3.	Gravel from soil developed on Upper Coal Measures ; river terrace.

The soils from which the pebbles were collected fall into two main groups which include all the gravelly soils of the area. These are :

(1) Soils related to the Red-brown Earths. This group of soils generally has a surface A_1 horizon of dark brown to dark grey-brown loam or clay-loam over a B_1 illuvial horizon of brown clay. Lime is sporadic and may or may not show an accumulation in the B_2 horizon. The deep subsoil (BC horizon) becomes gradually yellowish. G3–9, G11–15 and G17–18 all belong to this group, with some variation in the profile morphology, chiefly as regards colour of the B1 horizon, which varies from red-brown in G9 and G12 to dark brown in G3, 7, 14, 17, 18, and greyish yellow in G5. Most of the terrace soils fall into this group.

(2) Soils related to the Black Earths. These generally have a well structured dark brown clay surface which becomes browner with depth ; a zone of lime accumulation occurs in the BC horizon. G10 belongs to this group.

G16 was taken from the surface of a podsolic soil developed on the Muree Beds. The soil description has no significance because it is not a type represented on the river terraces.

EXAMINATION OF SAMPLES.

(*a*) Fundamental Properties. Sedimentary materials have a number of fundamental properties which can be used to provide data for descriptive purposes. Composition, size, shape and roundness of the pebble samples were examined by means of lithology counts, mechanical analysis (giving the variation in size of the pebbles and the amount of sorting), description of the roundness and sphericity.

Lithological Composition. Lithology counts of the kinds of rock in the pebbles contained in a conglomerate, river gravel or other material give precision to descriptions of these sediments, and if a sufficiently large number of samples is collected the results can be treated statistically. Conglomerates naturally vary somewhat in lithology from place to place even if belonging to the same bed. The diagnostic value of lithology counts is indicated in recently published papers by Allen (1949) and Plumley (1948). Materials which have been transported considerable distances will have lost their softer and more easily weatherable pebbles and will consist mainly of the most resistant types of rock such as quartz and chalcedony.

Mechanical Composition. One of the fundamental properties of sedimentary fragments is size, and the size distribution of the constituents is often

characteristic, e.g. in dune sands. The size is important in connexion with the action of the transporting agent. When all the fragments in a sediment are found within one or two grade-sizes the sediment is considered to be well sorted.

In describing conglomerates the proportion of pebbles to matrix is of interest as it is considered unlikely that a very fine-grained clayey matrix such as that present in the Lower Narrabeen conglomerate could be deposited at the same time as large pebbles, a decrease in stream or current velocity being indicated (Plumley, 1948, 544).

Roundness and Sphericity of Pebbles. Roundness is a measure of the curvature of the corners and edges of fragments, and is expressed as a ratio to the average curvature of the fragment as a whole, independent of its form. This is based on the curvature of surfaces as discussed by Thomson and Tait (1879, 101). Roundness indicates wear, probably by transport, but is difficult to interpret as different sized pieces of the same material in the same bed may, and generally do, show different degrees of roundness. Allen (1949, 310) states that the estimation of " roundness " is not yet satisfactorily measured for statistical treatment.

The shape is important in the selective transportation of fragments. Shape may be a useful feature when comparing pebbles believed to be from the same source and to have undergone similar conditions of transport. The final shape which rock materials will assume on continued wear has not yet been determined with any degree of certainty (Rayleigh, 1942 ; 1944). It is probably only homogenous material, fine and even grained, non-laminated, or from thick even beds among sedimentary rocks which will tend to assume a spherical shape. Observation of pebbles in a number of situations indicates that lamination, bedding and jointing are important original factors.

(b) Method of Examination.

Preliminary Treatment.

(i) *Conglomerates.* The field samples were carefully crushed in an iron mortar to free the pebbles from the matrix without breaking them. Some samples had a matrix harder than the pebbles and no unbroken pebbles could be obtained. The crushed material was quartered down until a representative sample of 2,000 to 3,000 gm. was obtained. All examinations were made on these samples.

(ii) *Gravelly Soils.* The pebbles were separated by washing out the soil and representative samples obtained as in (i).

Mechanical Analysis. The size composition of the pebbles in all samples was obtained by sieving through a set of sieves with square mesh openings of 1, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$ inch diameter (approximately 25, 12·5, 6·25 and 3 mm. respectively). These sizes fall within the Wentworth (1922) pebble grade, 64 −4 mm., with the exception of the smallest. It was not possible to obtain sieves giving the Wentworth scale which would have been desirable for comparison with pebbles described from other localities. The results of the mechanical analyses are given in Tables 3, 6 and 9. (All tables appear at the end of this paper.)

Lithology Counts. The rock types were identified in the −1+$\frac{1}{2}$ in. grade of the pebble samples from soils and Permian conglomerates, and in the −$\frac{1}{2}$+$\frac{1}{4}$ in. grade of the Lower Narrabeen conglomerates. The total number of pebbles present in each of these grades was identified, and amounted to between 100 and 150 in the soil pebble samples, and 50 to 100 in the conglomerates (see Tables 2, 5 and 8).

Determination of Roundness of Pebbles. The roundness of jasper, chalcedony and chert pebbles was determined in samples of the soils and Permian conglomerates, −1+$\frac{1}{2}$ in. grade with the exception of three samples, Nos. G1,

TABLE 2.

Lithology of Pebbles in the —⅛+¼ inch Grade, Lower Narrabeen Conglomerate.
(Percentage by Number.)

Sample No.	N6	N8	N9	N10	N11	N12	N14	N15
Rock types :								
Quartz	3	6	15	—	3	—	—	—
Jasper	10	6	8	23	10	15	4	—
Chert and chalcedony ..	46	63	38	38	41	49	46	65
Sedimentary*	36	22	38	38	45	20	22	34
Quartzite	—	—	—	—	—	—	1	—
Acid igneous†	—	1	—	—	—	15	21	—
Tuff	3	—	—	—	—	—	2	—

   * Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.
   † Acid igneous rocks include rhyolite, felsite and allied types.

TABLE 3.

Size Composition of Pebbles in the Lower Narrabeen Conglomerate.
(Grade units are in inches ; Percentage by weight.)

Grade.	—1+½.	—½+¼.	—¼+⅛.	—⅛ Coarse Sand +Matrix.
	%	%	%	%
Sample No.—				
N6	2·0	4·7	4·0	89·3
N7	—	—	2·5	97·5
N8	15·6	22·0	27·0	36·4
N9	3·4	3·0	0·5	93·1
N10	—	8·0	9·3	82·7
N12	21·0	33·0	18·0	28·0
N14	17·0	43·0	18·0	22·0
N15	15·0	31·0	23·0	31·0

TABLE 4.

Roundness and Sphericity of Pebbles from the Lower Narrabeen Conglomerate
(—½+¼ inch Grade).

	Mean Roundness.	Mean Sphericity.	Zingg Classification.*
Sample No.—			
N6	0·42	0·75	11
N8	0·54	0·78	1
N9	0·27	0·75	11
N10	0·40	0·76	11
N11	0·46	0·71	1
N12	0·50	0·74	11
N14†	0·52	0·75	11
N15	0·56	0·73	11

   * The shape of pebbles in Zingg's classification is : Class I, discs ; Class II, spherical ; Class III, blades ; Class IV, rod-like.
   † Chalcedony pebbles only.

G2 and G10, in which the acid igneous rock pebbles were used because of the low content of jasper and chalcedony. In the Lower Narrabeen conglomerates all the pebbles in the $-\frac{1}{2}+\frac{1}{4}$ in. grade were used. The roundness was determined visually by comparison with Krumbein's (1941) pebble images (see Tables 4, 7 and 10).

Shape of Pebbles. The shape was determined by Krumbein's intercept method (1941) which is based on a triaxial ellipsoid as the reference solid to which a pebble is compared (this implies that a sphere is the final shape towards which a pebble is progressing through abrasion, a fact which is not yet proved). It is therefore necessary to define the three diameters of a pebble as mutually perpendicular intercepts. The three diameters measured are designated as *a* (long), *b* (intermediate) and *c* (short). After the measurements have been made the ratios *b/a* and *c/b* are obtained and these are laid off on the axes of Krumbein's chart from which the sphericity figure is obtained. The Zingg (1935) pebble shape, based on the ratio of *b/a* to *c/b* is also given in Tables 4, 7 and 10. The measurements were made with a gauge similar to that illustrated by Krumbein (1941). An average of thirty randomly chosen pebbles of jasper and chalcedony from the $-1+\frac{1}{2}$ inch grade of soils and Permian conglomerates was measured to give the figures in Tables 7 and 10. Similar representative pebbles from the Lower Narrabeen conglomerates were used for the figures in Table 4.

<div align="center">DISCUSSION OF RESULTS.</div>

Lower Narrabeen Conglomerate.

The Triassic rocks of the district were first described by Carne (1906, 55), who noted the " chalcedonic and jasperoid constituents of the pebbles and boulders. Red and green are the predominant colours, whilst ordinary white quartz pebbles are rarer and smaller ". He considered that the pebbles were derived from altered Carboniferous and Devonian sediments to the north. On the other hand the Permian conglomerates are of quartz pebble character which distinguishes them from the Triassic conglomerates (*ibid.*, 53). Raggatt (1938), however, found difficulty in distinguishing the Permian from the Triassic conglomerates on lithological grounds alone. Dulhunty (1939) noted the presence of an upper portion about 250 ft. thick of homogenous medium-grained sandstone and a lower, 400 ft. thick, of conglomerate " being made up of coarse-grained sandstone packed with small rounded pebbles, mainly white quartz with a limited amount of red and black jasper " (*ibid.*, 32).

The Lower Narrabeen conglomerate was sampled at the base, middle and top of the lower portion of these Triassic beds. When examined in hand specimen, the basal Narrabeen conglomerate between Murrurundi and Denman is seen to be massive with a fine-grained, firmly cemented, clayey matrix which encloses pebbles of chalcedony, jasper, clayey sandstone and quartz, varying in size from about one-eighth inch to over one inch in diameter, the majority being about one-half inch in diameter. The matrix is very seldom sandy, and may be so hard that it is impossible to remove pebbles without breaking them. From this it may vary to softer material and finally to sandy lenses with few pebbles. On superficial examination the bed appears to be fairly uniform both laterally and vertically, but the mechanical analyses indicate that this is not so. On weathering the softer pebbles and matrix are removed first, leaving jasper and chalcedony prominent. The lithological composition is given in Table 2, which shows that chert and chalcedony are the most abundant constituents, followed by various sedimentary rocks. Quartz is not abundant except in N9 ; only two samples, N12 and N14, contain appreciable amounts of acid igneous rock pebbles. Jasper is always more plentiful than black chert ; greenish cherty pebbles which are so noticeable on weathered surfaces are not plentiful.

The variation in lithology of the pebbles in the Lower Narrabeen conglomerate can be shown thus :

Types of Pebbles.
(Percentage by Number.)

		Quartz.	Jasper.		Chalcedony.	Sedimentary.	Acid Igneous.
Upper ..	..	10	7	(57)	50	30	½
Middle ..	..	—	13	(55)	42	30	10
Lower ..	..	1½	9	(59)	50	34	5

These figures are the averages of only a limited number of samples, but the ratio of jasper plus chalcedony to sedimentary rocks appears to be rather constant, and can be taken as characteristic of these beds.

Table 3 gives the distribution of sizes of the pebbles for the same samples and the variation in proportion of pebbles to matrix. It is unsafe to generalise from few samples, but the basal part of these beds appears to have a larger pebble content than the upper.

The mean roundness and mean sphericity are given in Table 4. Although the first impression given by the pebbles is that of roundness, close examination of the edges indicates that the rounding is only moderate when compared with Krumbein's roundness images (1941, Pl. 1). Individual pebbles may reach a roundness of $0 \cdot 8$ or $0 \cdot 9$, but the mean is between $0 \cdot 42$ and $0 \cdot 56$, with one sample, N9, having a roundness of only $0 \cdot 27$, which indicates sharp broken edges (care was taken during the initial crushing not to break pebbles so that this figure is a natural one).

The shape of the pebbles, given as mean sphericity, is much more uniform than the roundness ; it varies between $0 \cdot 71$ and $0 \cdot 78$, the pebbles falling into Zingg's (1935) spherical class, with the exception of N8 and N11, which are disc-like. The pebbles measured were largely chalcedony, which, being homogenous, would tend to assume a spherical form rather than any other.

Permian Conglomerates.

The Permian conglomerates are represented by samples G1 and G2 from the Upper Coal Measures, G13 from the Branxton Beds, G16 from the Muree Beds, and G17 from the Greta Coal Measures (see Table 1). The distribution and lithology of these formations in the Upper Hunter River Valley has been described by Raggatt (1929 ; 1938). The Muree Beds have the greatest surface area.

The lithology of these samples is given in Table 5. The Upper Coal Measure beds are characterised by the absence of quartz and jasper, the limited quantity

TABLE 5.

Lithology of Pebbles in the $-1+\frac{1}{2}$ in. Grade from Permian Conglomerates.
(Percentage by number.)

Sample No.	G1.	G2.	G13.	G16.	G.17
Rock types—					
Quartz	—	—	—	9	—
Jasper	—	—	21	27	—
Chalcedony and chert ..	3	7	10	5	39
Sedimentary*	16	3	40	59	18
Quartzite	—	7	—	—	2
Acid igneous†	81	69	28	—	24
Basalt	—	14	1	—	—

* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.
† Acid igneous rocks include rhyolite, felsite and allied types.

of chalcedony, the rather small quantity of sedimentary rock pebbles, and the preponderance of acid igneous rock pebbles. The basalt pebbles in G2 may be due to contamination. The sample from the Branxton Bed is characterised by jasper and chalcedony, but the most prominent constituent is sedimentary

TABLE 6.

Size Composition of Pebbles in the Permian Conglomerates.
(Grade units in inches ; percentage by weight.)

Grade	—2+1.	—1+½.	—½+¼.	—¼+⅛.	—⅛ (Coarse Sand and Matrix).
Sample No.—	%	%	%	%	%
G1	20·0	13·0	41·0	18·0	8·0
G2	66·4	25·1	4·0	1·1	3·3
G13	52·5	35·7	11·8	—	—
G16	9·6	19·0	47·8	4·2	19·1
G17	24·5	28·6	37·6	7·0	2·2

TABLE 7.

Roundness and Sphericity of Pebbles from the Permian Conglomerate
(—1+½ inch Grade).

	Mean Roundness.	Mean Sphericity.	Zingg Classification.*
Sample No.—			
G1†	0·50	0·78	11
G2†	0·55	0·77	11
G13	0·49	0·86	11
G16	0·44	0·76	11
G17	0·55	0·77	11

* The shape of pebbles in Zingg's classification is : Class I, discs ; Class II, spherical ; Class III, blades ; Class IV, rod-like.

† Acid igneous rock pebbles ; the remainder are jasper and chalcedony pebbles.

TABLE 8.

Lithology of Pebbles in the —1+½ in. Grade of River Terrace Soils.
(Percentage by Number.)

Sample No.	G3.	G4.	G5.	G6.	G7.	G8.	G9.	G10.	G11.	G12.	G14.	G15.	G18.
Rock types—													
Quartz	3	5	3	—	4	4	5	2	16	6	—	2	6.
Jasper	4	10	15	—	8	14	15	—	26	4	2	31	29
Chalcedony and chert	37	75	64	69	40	79	54	6	35	67	42	31	9
Sedimentary* ..	13	3	3	15	9	2	12	13	11	14	22	21	1
Quartzite	—	—	—	—	—	—	—	—	—	—	—	—	1
Acid igneous†	29	6	10	16	33	—	12	34	12	8	29	14	27
Basalt	12	1	3	—	5	1	3	37	2	—	4	—	26

* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.

† Acid igneous rocks include rhyolite, felsite and allied types.

rock ; acid igneous rock pebbles are also prominent. The Muree Bed contains quartz, jasper, chalcedony and sedimentary pebbles but no acid igneous rocks, whereas the Greta Coal Measure conglomerate has conspicuous igneous rock pebbles with no quartz and jasper, although chert and chalcedony pebbles are plentiful.

The variation in size of the pebbles is given in Table 6. G2 (Upper Coal Measures) and G13 (Branxton Beds) are fairly well graded, but the pebbles of other samples are not. In G2 and G13 the maximum grade is in the $-2+1$ inch grade. A slight maximum occurs in the other samples in the $-\frac{1}{2}+\frac{1}{4}$ inch grade. The percentage of coarse sand and matrix is conspicuous only in G16 (Muree).

The mean roundness and sphericity are given in Table 7. The mean roundness varies from 0·44 (Muree) to 0·55 (Upper Coal Measures and Greta). The sphericity varies from 0·77 (Upper Coal Measures and Greta) to 0·86 (Branxton). The pebbles from all these samples fall into Zingg's (1935) spherical class.

River Terrace Soils.

The soils from which pebbles were obtained are described in the Introduction. All the samples with the exception of G10 were from Red-brown Earth on the river terraces.

The lithology is given in Table 8, which is a simplification of the rock types actually recorded, which are : quartz (milky), chalcedony and chert (red, white, grey, banded), jasper, quartzite, shale (white, grey, indurated), sandstone (coarse, fine, brown, yellow, ferruginous, clayey, chalky), claystone, ferruginous mudstone, tuff, acid igneous (mainly lavas ; coarse, fine, altered, white, pale green, banded), rhyolite, porphyry, basalt, weathered basalt. There is thus a much greater variety in the gravels than in the Lower Narrabeen conglomerate.

Quartz is present in all but two of the samples in small amounts only, and is conspicuous (16%) in G11 collected from above the Upper Coal Measures.

Jasper and chalcedony are prominent constituents in all the samples except G10. The range is from 38% to 93% (G8 from near Scone). G3, G7, G14, G18 are low in jasper and chalcedony and high in acid igneous rocks (when compared with other samples from the area) :

	G3. %	G7. %	G14. %	G18. %
Jasper and chalcedony	41	48	44	38
Acid igneous ..	29	33	29	27

These samples were all collected from above the Upper Coal Measures and Branxton Beds whose jasper and chalcedony contents are rather low and acid igneous rock contents rather high. It may be presumed therefore that the parent material of the soil is in part at least the underlying rock.

Of those samples with a high percentage of jasper and chalcedony a number contain varying percentages of acid igneous rock pebbles up to 12% in G9 and G11. The large amount of jasper and chalcedony appears to have been added to the original weathering product of the Upper Coal Measures and other beds, although contamination with material from the Muree Beds might have the same effect.

Sedimentary rock pebbles occur in practically all of these samples and their source could be any of the Permian beds in the valley. Table 5 shows that the Muree beds contained nearly 60% of this type of pebble. The largest percentages of sedimentary rock pebbles occur in those samples rather low in jasper and chalcedony and therefore strengthens the case for rather less contamination of these samples.

Basalt pebbles occur in small amounts in a number of these samples, G18 containing 26% and G3, 12%. G6, G12 and G15 contain no basalt, and the remaining samples only small amounts. In view of the fact that one of the

TABLE 9.

Size Composition of Pebbles in the River Terrace Soils.
(Grade units in inches; percentage by weight.)

Grade	$-2+1.$	$-1+\frac{1}{2}.$	$-\frac{1}{2}+\frac{1}{4}.$	$-\frac{1}{4}+\frac{1}{8}.$	$-\frac{1}{8}$ (Coarse Sand and Fine Sand).
	%	%	%	%	%
Sample No.—					
G3 ..	42·2	21·0	25·0	6·4	5·4
G4 ..	44·8	25·0	21·7	4·0	4·3
G5 ..	4·1	16·8	26·0	15·9	35·2
G6 ..	33·0	37·4	18·5	4·8	6·3
G7 ..	57·8	21·5	11·6	2·7	4·7
G8 ..	26·5	23·4	44·8	7·0	7·6
G9 ..	55·5	30·3	11·1	1·0	1·9
G10	62·5	26·1	6·2	1·4	4·0
G11	27·5	32·0	32·1	7·7	—
G12	57·5	23·1	14·3	2·5	2·4
G14	91·3	8·7	—	—	—
G15	47·7	19·1	17·6	5·6	10·9
G18	76·0	24·0	—	—	—

Upper Coal Measure conglomerates contained basalt pebbles it seems probable that little significance can be attached to small quantities of basalt in these samples, whereas large quantities indicate either proximity to basaltic flow remnants, plugs or sills, or to addition by stream transport of pebbles from an

TABLE 10.

Roundness and Sphericity of Pebbles from the River Terrace Soils ($-1+\frac{1}{2}$ in. Grade; Jasper and Chalcedony).

	Mean Roundness.	Mean Sphericity.	Zingg Classification.*
Sample No.—			
G3 ..	0·48	0·72	II
G4 ..	0·48	0·73	II
G5 ..	0·46	0·76	II
G6 ..	0·47	0·73	II
G7 ..	0·51	0·76	II
G8 ..	0·53	0·77	II
G9 ..	0·52	0·76	II
G10† ..	0·33	0·73	II
G11 ..	0·50	0·78	II
G12 ..	0·51	0·73	II
G14 ..	0·49	0·77	II
G15 ..	0·52	0·78	II
G18 ..	0·55	0·75	II

    * The shape of pebbles in Zingg's classification is : Class I, discs ; Class II, spherical ; Class III, blades ; Class IV, rod-like.
      † Acid igneous rock pebbles.

outcrop of basalt. Many of the basalt pebbles in these soils are weathered, and it is possible that many originally present may have disappeared during soil formation.

The only soil belonging to the Black Earth group (G10) contains very little quartz and chalcedony, but 37% of basaltic pebbles and 34% of acid igneous rock pebbles. As this sample was collected from near the junction of the Pages and Upper Hunter Rivers, it is possible that the basaltic pebbles have been transported there. The influence of the basalt is clearly to be traced in the formation of a Black Earth. If the basalt were *in situ*, it is probable that acid igneous rock pebbles would not be present.

The variation of sizes of the pebbles is given in Table 9. In general the pebbles are not well sorted except in G14 and G18, with a maximum of 91% and 76% in the $-2+1$ inch grade. These are most probably river gravels, as the grading of the Permian sediments is not particularly good. G7, G9, G10, G12 also show a fairly strong maximum in the same grade. The Permian conglomerates also show a maximum in this grade, where sorting is at all good, but the Lower Narrabeen conglomerates examined here are much finer grained with a maximum in the $-1+\frac{1}{2}$ or $-\frac{1}{2}+\frac{1}{4}$ inch grade. Without additional samples it would be unwise to generalise further from these figures.

Figures for the roundness and sphericity are given in Table 10. The roundness for pebbles from the Red-brown earth soils varies from $0\cdot46$ to $0\cdot55$, which indicates that the edges are not at all well-rounded and that many broken pebbles are present. The mean roundness for sample G10 is only $0\cdot33$. The mean sphericity is fairly constantly high, ranging from $0\cdot72$ to $0\cdot78$. It appears to have little diagnostic value, except to indicate similarity, in this series of samples. All the pebbles fall into Zingg's spherical class. It would appear that the same kind of environment existed for all these pebbles, though the homogenous material (jasper and chalcedony) would tend to assume this shape on abrasion irrespective of environment.

CONCLUSIONS.

The number of samples examined was insufficient to treat the results statistically, but the following conclusions appear to be justified.

Detailed lithological examination of the various conglomerates has given precision to the description of these beds, and this information can be used to suggest the origin of the various gravelly soils which have developed on the river terraces in the area examined. Further evidence is expected from an examination of the heavy mineral residues of these soils. Contamination with material either from the Lower Narrabeen conglomerate or the resorting and redistribution of the materials of the Permian beds is indicated. Acid igneous rock pebbles appear to be derived from various members of the Permian in a number of instances. The presence of basalt pebbles indicates either nearness to source or transport from a source at no great distance. The degree of sorting of several of the terrace gravels indicates the action of rivers, but it seems that transport was not for long distances, as no pebbles from the Kuttung glacial beds were found. Little can be inferred from the figures for roundness and sphericity; the pebbles are not as well water-worn as previous descriptions indicate, which shows that transport has not been from long distances or continuous. It is probable that no further alteration of shape or roundness has been made by the action of the Upper Hunter and its tributaries. All the pebbles are of the same type except some of those in the Lower Narrabeen conglomerates which are, in addition, simpler lithologically. It is suggested that the weathering *in situ* of the Permian beds is an important factor in the soils·developed on the terraces in some localities.

ACKNOWLEDGEMENTS.

REFERENCES.

Allen, P., 1949. *Quart. J. geol. Soc. Lond.*, **104**, 257.

Browne, W. R., 1924. THIS JOURNAL, **58**, 128.

Carne, J. E., 1906. *Mem. geol. Surv. N.S.W.*, No. 6.

David, T. W. E., 1907. *Mem. geol. Surv. N.S.W.*, No. 4.

Dulhunty, J. A., 1939. THIS JOURNAL, **73**, 29.

Krumbein, W. C., 1941. *J. Sed. Petrol.*, **11**, 64.

Plumley, W. J., 1948. *J. Geol.*, **56**, 526.

Raggatt, H. G., 1929. *A.R. Dept. Mines N.S.W.*, 100.

————————— 1939. D.Sc. Thesis. (Unpublished.)

Rayleigh, Lord, 1942. *Proc. Roy. Soc. A.*, **181**, 107.

————————— 1944. *Nature*, **154**, No. 3901, 169.

Sussmilch, C. A., 1940. *Proc. Linn. Soc. N.S.W.*, **65**, 301.

Thomson, W., and Tait, P. G., 1879. Treatise on Natural Philosophy.

Wentworth, C. K., 1922. *J. Geol.*, **30**, 377.

Zingg, T., 1935. *Schweiz. Min. Pet. Mitt.*, **15**, 39.

THE RESOLUTION OF THE TRIS o,PHENANTHROLINE FERROUS ION AND THE OXIDATION OF THE ENANTIOMORPHOUS FORMS.

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When o,phenanthroline is added to ferrous salt solutions, red compounds result which have been shown to have the constitution $Fe(phenan)_3X_2.nH_2O$ (Blau, 1898). The tris o,phenanthroline ferrous ion is reversibly oxidisable to the blue tris o,phenanthroline ferric ion the redox potential for the reaction

$$Fe(phenan)_3{}^{++}-e' \rightarrow Fe(phenan)_3{}^{+++}$$

being 1·12 volts (Smith and Richter, 1944; Dwyer and McKenzie, 1947). In this paper the resolution of the ferrous complex and the oxidation of the enantiomorphous forms is described.

The resolution was carried out through the antimonyl tartrates, and it was found that on adding potassium antimonyl tartrate to a racemic solution of $Fe(phenan)_3{}^{++}$ in water the l-complex d-antimonyl tartrate separated as a highly insoluble precipitate, whilst the d-complex remained in solution and could be precipitated from the mother liquid as the sparingly soluble perchlorate. The perchlorate of the laevo form was obtained by dissolving the antimonyl tartrate precipitate in caustic soda solution (thus destroying the antimonyl tartrate radicle) and adding sodium perchlorate. The active perchlorates were more soluble in water than the racemate.

The resolution of the analogous tris o,phenanthroline ruthenium II and nickel II complexes and recently that of the osmium II complex has been carried out in a similar way (Dwyer and Gyarfas, 1949a, b, c). In all of these complexes the d-Me(phenan)$_3$ d-antimonyl tartrate (Me = Ru II, Ni II, Os II), formed the highly insoluble compound. It is reasonable to suppose, therefore, that the form of the ferrous complex precipitated as the d-antimonyl tartrate has the same configuration as the dextrorotatory Ru II, Ni II and Os II complexes. The sign of the rotation is of no significance since all these ions possess a strongly abnormal rotatory dispersion, the investigation of which is now being carried out, and will be published in a subsequent communication.

The optical forms were more stable than the active forms of the tris 2 : 2′ dipyridyl ferrous ion resolved by Werner (1912a). Thus whilst the rotations of solutions of this substance dropped to half of its original value in half an hour the phenanthroline complexes in solution have a half life of approximately one hour, and the solids possess some rotation even after a period of six months. The same relation was found between the stabilities of the corresponding $Ni(dipy)_3{}^{++}$ and $Ni(phenan)_3{}^{++}$ complexes (Morgan and Burstall, 1931; Dwyer and Gyarfas, 1949b). On standing from a racemic solution of the ferrous complex containing excess antimonyl tartrate, the whole of the complex precipitated slowly as the l-complex d-antimonyl tartrate, leaving a colourless solution behind. This is due to the racemisation of the solution. The equilibrium between the d and l complex ions is being shifted towards the latter, which is continuously eliminated from the solution as the insoluble antimonyl

tartrate, and finally none of the d-complex remains. A similar reaction was, observed on the resolution of the trioxalato chromiates with strychnine (Werner 1912b).

In a previous paper (Dwyer and Gyarfas, 1949a), the oxidation of the enantiomorphous forms of the tris o,phenanthroline ruthenium II complex was described. It was found that on oxidation of the active solutions of this complex the solutions of the blue ruthenium III complex were still optically active, although the magnitude of rotation was different, and that on reduction the ruthenium II complex was obtained with its rotation unchanged. If the same experiment is carried out on the active tris o,phenanthroline ferrous ion at room temperature, as stated by the authors in a note in *Nature* (Dwyer and Gyarfas, 1949), the rotation is lost on oxidation due to the rapid racemisation of the ferric complex. However, at 6° C. the rate of racemisation being reduced, active solutions of the ferric complex could be obtained. The rate of racemisation even at 6° C. was too rapid to permit measurement of the specific rotation with any degree of accuracy, but it is approximately 60% of that of the ferrous complex in the NaD line.

EXPERIMENTAL.

Owing to the racemisation of the active substances standard solutions could not be made up for measurements of rotations. The determinations of specific rotations was done by shaking the active substance in ice-cold water for a few seconds, filtering off the undissolved material on the filter pump, and measuring the angle of rotation immediately. The concentration of the solution was determined subsequently by comparing it with a standard solution in a photo-electric colorimeter.

A 2 dm. tube was used in all experiments.

l-Tris o,Phenanthroline Iron II d-Antimonyl Tartrate Tetrahydrate.

d,l Tris o,phenanthroline ferrous sulphate was prepared by the addition of finely divided o,phenanthroline monohydrate (2·2 g.) to a solution of ferrous sulphate heptahydrate (1·2 g.) in water (100 ml.). The mixture was stirred until the phenanthroline had dissolved completely. To the deep red solution of tris o,phenanthroline ferrous sulphate a solution of potassium d-antimonyl tartrate (2·5 g.) in water (20 ml.) was added slowly. On scratching the sides of the vessel a dark red crystalline substance was obtained. The reaction mixture was cooled rapidly in ice and the precipitate filtered off immediately. The crystalline substance was found to be pure l-tris o,phenanthroline ferrous d-antimonyl tartrate. It was practically insoluble in water but could be recrystallised by solution in 0·1 N caustic soda (50 ml.) and reprecipitation with the addition of acetic acid and a little potassium antimonyl tartrate. The substance crystallised in dark red needles.

A 0·0100% solution in water gave $\alpha_D = -0·19°$, whence $[\alpha]_D^6 = -950°$.

Found : Fe = 4·37% ; Sb = 19·54%.

Calculated for $[Fe(C_{12}H_8N_2)_3](SbO.C_4H_4O_6)_2.4H_2O$: Fe = 4·50% ; Sb = 19·63%.

l-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.

The l-tris o,phenanthroline ferrous d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 ml.) by shaking at about 5° C., and the solution filtered. Sodium perchlorate solution was then added slowly and on scratching the sides of the vessel a red crystalline precipitate was obtained. This, after immediate filtration, washing with ice water and drying, gave the pure l-perchlorate in microprismatic needles. The substance was appreciably soluble in water, very soluble in acetone and sparingly soluble in alcohol.

A 0·0144% solution in water gave $\alpha_D = -0·41°$, and a 0·0126% solution in water gave $\alpha_D = -0·35^{5°}$, whence $[\alpha]_D^6 = -1416°$.

Found : Fe = 6·53% ; N = 10·04%.

Calculated for $[Fe(C_{12}H_8N_2)_3](ClO_4)_2.3H_2O$: Fe = 6·58% ; N = 9·90%.

d-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.

The mother liquid of the original precipitate with potassium antimonyl tartrate was strongly dextrorotatory. The cold solution (5° C.) was treated immediately with sodium perchlorate solution. (Avoiding an excess to prevent the precipitation of potassium perchlorate.) The resulting red crystalline precipitate was the pure perchlorate of the dextro complex forming microprisms and needles.

A $0 \cdot 0111\%$ solution in water gave $\alpha D = +0 \cdot 32°$ and a $0 \cdot 0123\%$ solution in water gave $\alpha D = +0 \cdot 35°$, whence $[\alpha]_D^6 = +1432°$.

Found : Fe $= 6 \cdot 53\%$.

Calculated for $[Fe(C_{12}H_8N_2)_3](ClO_4)_2.3H_2O$: Fe $= 6 \cdot 58\%$.

SUMMARY.

Tris o,phenanthroline iron II perchlorate has been resolved through the d-antimonyl tartrate. The optical forms were stable in the solid state for some months, but racemised rapidly in solution. After oxidation of the enantio-morphous forms with ceric sulphate at 6° C., the resulting blue iron III complex was found to possess a fleeting activity.

REFERENCES.

Blau, 1898. *Monatsch,* **19,** 647.

Dwyer and McKenzie, 1947. THIS JOURNAL, **81,** 93.

Dwyer and Gyarfas, 1949*a*. *Ibid.,* **83,** 000.

——————— 1949*b*. *Ibid.,* **83,** 000.

——————— 1949*c*. Unpublished work.

——————— 1949. *Nature,* **163,** 918.

Morgan and Burstall, 1931. *J. Chem. Soc.,* 2213.

Smith and Richter, 1944. *Ind. Eng. Chem. Anal. Ed.,* **16,** 580.

Werner, 1912*a*. *Ber.,* **45,** 433.

———— 1912*b*. *Ibid.,* **45,** 3061.

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A NOTE ON SOME 4–METHOXYBENZENEAZO DERIVATIVES OF RESORCINOL

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On coupling molar equivalents of diazotised p-anisidine with resorcinol monacetate in alkaline solution, both a mono- (I, 33%) and a bis-azo compound (II, 29%) were obtained, but no appreciable amounts of acetyl derivatives could be isolated. The same two products were also isolated (I, 47%; II, 17%) by coupling molar proportions of diazotised p-anisidine with resorcinol in the presence of alkali. (I) must be 2 : 4-dihydroxy-4'-methoxyazobenzene.

The formation of bis-azo compounds by coupling diazotised aniline with resorcinol was first reported by Wallach and Fischer (1882) (cf. Typke, 1877; Will and Pukall, 1887). It was later found that the pH of the solution determines which of two bis-azo isomers is formed. In the presence of sodium carbonate or acetate, 2 moles of diazotised aniline couple with one of resorcinol to give 2 : 4-bis(benzeneazo)-1 : 3-dihydroxybenzene (Kostanecki, 1888; cf. Liebermann and Kostanecki, 1884; Kostanecki, 1887; Orndorff and Ray, 1907), whilst in dilute excess sodium hydroxide 4 : 6-bis(benzeneazo)-1 : 3-dihydroxybenzene is formed (Kostanecki, 1888).

It is thus reasonable to assume that the structure of the bis-azo compound (II) formed above is 4 : 6-bis(4'-methoxybenzeneazo)-1 : 3-dihydroxybenzene.

On coupling molar proportions of diazotised p-anisidine with resorcinol monomethyl ether, two compounds $C_{14}H_{14}O_3N_2$ are formed (cf. Hodgson et al., 1934). One isomer, m.p. 116°, occurs to about 90%, the other, m.p. 134°, to about 10% in the mixture. Separation was achieved by exhaustive steam distillation, the higher melting isomer being slightly volatile. This isomer probably identical with the hydroxyazo compound, m.p. 121° (crude), isolated by Cumming and Ferrier (1925) from 4 : 4'-dimethoxyazoxybenzene by the action of light, is therefore 2-hydroxy-4 : 4'-dimethoxyazobenzene (III). The other isomer, m.p. 116°, would then be 4-hydroxy-2 : 4'-dimethoxyazobenzene (IV).

On methylation with diazomethane of (I) yields of (III) (68%) and (IV) (26%) were obtained. This result is to be expected from a hydrogen bonded o-hydroxyazo compound.

EXPERIMENTAL.

4'-methoxy-2 : 4-dihydroxyazobenzene (I), and *4 : 6-bis(4'-methoxybenzeneazo)-1 : 3-dihydroxy-benzene* (II)

(A) p-Anisidine (1 mol.) was diazotised in hydrochloric acid (3 mol.) in the usual way, and added to a freshly prepared dilute solution of resorcinol monacetate (1 mol.) in sodium hydroxide (5 mol.) at 0° C. After stirring for 30 min., the solution was made faintly acid, and the red-brown precipitate filtered off. Extraction with hot 20% acetic acid removed (I), which crystallised out on cooling, and after recrystallisation from dilute acetic acid, formed glistening carmine needles (33%), m.p. 150°, which became dull orange needles, m.p. 150–151°, on drying in the desiccator, or at 110°.

Found: N, 11·8; –OMe, 12·9%.

Calculated for $C_{18}H_{18}O_3N_2$: N, 11·5; –OMe, 12·7%.

The residue (II) crystallised from glacial acetic acid in minute brown-violet flakes, m.p. 225°, yield 29%.

Found: N, 14·8; –OMe, 16·1%.

Calculated for $C_{20}H_{18}O_4N_4$: N, 14·8; –OMe, 16·4%.

(B) Preparation as above, using resorcinol instead of its monacetate. Yields: (I), 47%; (II), 17%.

4 : 6-Bis(4'-methoxybenzeneazo)-1 : 3-dimethoxybenzene (V).

(V) was formed by methylation of (II) in boiling acetone solution with excess methyl iodide in the presence of potassium carbonate. It formed red needles from dilute acetic acid.

Found: N, 13·8%.

Calculated for $C_{22}H_{22}O_4N_4$: N, 13·8%.

2-Hydroxy-4 : 4'-dimethoxyazobenzene (III) and *4-hydroxy-2 : 4'-dimethoxyazobenzene* (IV).

Preparation as for (I) and (II), using resorcinol monomethyl ether instead of resorcinol monacetate. Before acidification, the solution was extracted with ether, which removed a small quantity of red crystals of (III) (m.p., after one crystallisation from aqueous acetic acid, 127–128°). Another crop of (III) (total 5%) was obtained by acidification of the liquor, followed by exhaustive steam distillation. (III) forms glistening red monoclinic crystals from aqueous alcohol or dilute acetic acid, m.p. 134°.

Found: N, 10·8%.

Calculated for $C_{14}H_{14}O_3N_2$: N, 10·9%.

It is only slightly soluble in cold 0·5% to 10% sodium hydroxide solution.

The steam distillation residue affords (IV) (60%) after three crystallisations from aqueous acetic acid, aqueous alcohol or aqueous pyridine. From the former it crystallises in red needles, m.p. 85°, which after drying lose their solvent of crystallisation and become dull salmon coloured, m.p. 116°.

Found: N, 11·0%; –OMe, 23·9%.

Calculated for $C_{14}H_{14}O_3N_2$: N, 10·9%; –OMe, 24·3%.

The *benzoyl derivative* crystallises from dilute acetic acid in shimmering orange-brown flakes, m.p. 144·5°.

Found: N, 7·8%; –OMe, 16·7%.

Calculated for $C_{21}H_{18}O_4N_2$: N, 7·7%; –OMe, 17·1%.

Methylation of (I).

(I) (0·25 g.) in dry ether (50 ml.) was treated with a solution of a large excess of diazomethane (from nitrosomethylurea, 2 g.) in ether (50 ml.), and allowed to stand overnight. The filtered solution was extracted three times with 10% sodium hydroxide solution (20 ml.). The alkali extract afforded (IV) (impure, 0·07 g., 26%), the ether extract (III) (pure, 0·18 g., 68%).

REFERENCES.

Cumming, W. M., and Ferrier, G. S., 1925. *J. chem. Soc.*, **127**, 2374.
Hodgson, H. H., Dyson, R. J. H., and Bell, H., 1934. *Ibid.*, 629.
Kostanecki, S. von, 1887. *Ber.*, **20**, 3133.
————————— 1888. *Ibid.*, **21**, 3114.
Liebermann, C., and Kostanecki, S. von, 1884. *Ibid.*, **17**, 876.
Orndorff, W. R., and Ray, B. J., 1907. *Ibid.*, **40**, 3211.
Typke, P. G. W., 1877. *Ibid.*, **10**, 1576.
Wallach, O., and Fischer B., 1882. *Ibid.*, **15**, 2814.
Will, W., and Pukall, W., 1887. *Ibid.*, **20**, 1119.

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STUDIES IN THE DEMETHYLATION OF THIOANISOLE.

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During attempts to prepare the sulphur analogues of the synthetic sex hormones stilbestrol, hexestrol and dienestrol it was not found possible to demethylate the intermediate methyl ethers and experiments were begun on the dealkylation of thioanisole (Hughes and Thompson, 1948). This paper reports further attempts using the methods successfully used with oxygen alkyl ethers.

Sodium in boiling pyridine, as used by Prey (1943) for the cleavage of phenol ethers, gave 60% thiophenol and no thioanisole was recovered.

Heating with aluminium chloride caused some demethylation, but the yields of thiophenol were low and were difficult to reproduce. With equimolecular amounts of thioanisole and aluminium chloride at 100° C. the yield of thiophenol averaged 20%, in one experiment 35% was obtained. Thioanisole was always recovered mixed with higher boiling fractions, which may contain alkylated thioanisoles (*cf*. Baddeley, 1944).

The stability of aliphatic sulphides to aluminium chloride has previously been noted by Lee and Dougherty (1939), who found that *n*-amyl sulphide was unaffected by two hours' refluxing with aluminium chloride in benzene solution. Auwers and Arndt (1909) were unable to demethylate 2-aceto-4-methyl thioanisole with aluminium chloride, but Harnish and Tarbell (1948) showed that the more labile phenyl benzyl sulphide gave 21% debenzylation when treated at 50° C. for twenty-four hours with the same reagent.

Alcoholic potash which demethylates anisole slowly at 200° C. had no appreciable effect on thioanisole after seven hours at 230° C.

Thus from the above and previous results (Hughes and Thompson, *loc. cit.*) it is obvious that thioanisole is much more resistant to both acidic and basic reagents than is anisole. The effects of the reagents used are shown in the following table.

Reagent.	Reaction Conditions.	Percentage Yield of Demethylated Product.	
		Anisole.	Thioanisole.
Hydriodic acid, hydrobromic acid ..	2 hr. 130° C.	100	0
Pyridine hydrochloride	6 hr. 200° C.	100	0
Magnesium iodide	1 hr. 200° C.	58	0
Aluminium chloride	2 hr. 100° C.	100	20
Caustic potash in ethanol	7 hr. 200° C.	7	0
Sodium in pyridine	5 hr. 120° C.	94	62
Sodium in ammonia	7 hr.	27 (Birch, 1947)	100
	15 hr.	100*	100

The generally accepted mechanism for acid demethylation of ethers is shown in the following equation (Remick, 1942).

$$R\text{--}\overset{..}{\underset{..}{O}}\diagdown_{CH_3} + H^+ + Br^- \rightarrow [R\text{--}\overset{..}{O}\ldots H]^+Br^- \rightarrow R\text{--}O\text{--}H + CH_3Br$$
$$\underset{CH_3}{}$$

The proton addition is based on the well-known existence of H_3O^+ and $(C_2H_5)_2O.HCl$.

However, the properties of divalent sulphur reveal that proton addition is extremely weak and the slight evidence for the existence of compounds such as $(C_2H_5)_2S.HCl$ and H_3S^+ (Bagster, 1911 ; Jablczynska-Jedrzejewska and Groyecka, 1937) suggests that the analogous process

$$R\text{--}\overset{..}{\underset{..}{S}}\diagdown_{CH_3} + H^+ + Br^- \rightarrow [R\text{--}\overset{..}{S}\ldots H]^+Br^-$$
$$\underset{CH_3}{}$$

would be much less likely, and if this is the rate controlling step, then the reaction would be very slow. Furthermore, Fehnel and Carmack (1949) have presented evidence for the polarisation of the phenylmercapto group in which the benzene ring acts as an electron donor to the sulphur atom as shown in the following structures.

This would compensate for any loss of electron density on the sulphur atom (after the addition of the proton) and thus prevent the weakening of the sulphur carbon bond. Resonance involving these structures cannot occur with ethers as oxygen cannot expand its valency shell.

However, it is well known that sulphides co-ordinate readily with alkyl halides to form sulphonium salts while there is apparently no evidence for a similar reaction with ethers ; sulphides also co-ordinate readily with oxygen to form sulphoxides and sulphones, and with halides of mercury and platinum metals, and it is reasonable to assume that this is why aluminium chloride will split thioethers, although here too the weakening of the sulphur-carbon bond is much less than is the case with the oxygen-carbon bond.

$$R\text{--}\overset{..}{\underset{..}{S}}\diagdown_{CH_3} + AlCl_3 \rightarrow [R\text{--}\overset{..}{S}\text{--}CH_3] \rightarrow R\text{--}S\text{--}AlCl_2 + CH_3Cl$$
$$\underset{AlCl_3}{}$$

With alcoholic alkali the effective reagents must be the hydroxyl or ethoxyl ions which exert a nucleophilic attack on the carbon atom. The greater polarity of the carbon atom in anisole, due to the greater electron attracting power of oxygen, should make it more easily attacked, which is in accord with the experimental results.

$$R\text{--}\overset{\delta-}{O}\diagdown_{CH_3} \overset{\delta+}{} + OH^- \rightarrow [R\text{--}O\ldots CH_3\ldots OH]^- \rightarrow R\text{--}O^- + CH_3OH$$

(If this is the mechanism for the alkaline hydrolysis it is difficult to understand why anisole metalates in the *ortho* position with butyl lithium, whereas thioanisole undergoes lateral metalation (Gilman and Webb, 1940)).

The difference in the stability of the sulphur and oxygen alkyl linkages suggested the possibility of the transfer of the methyl group from anisole to thiophenol. As expected, when anisole and thiophenol were heated in the presence of hydriodic acid no transfer occurred, the anisole being demethylated in the normal way.

However, in the presence of alcoholic potash the thiophenoxide ion caused complete demethylation of anisole after six hours' heating at 200° C. In the absence of thiophenol the yield of phenol under the same conditions was only 7%. Stoemer and Kahlert (1901) obtained 12% phenol after fifteen hours.

The reaction apparently involves a nucleophilic attack on the carbon atom and proceeds as follows because none of the otherwise expected intermediate products will methylate thiophenol under these conditions, and although the reaction was carried out in ethanol only thioanisole was obtained.

$$C_6H_5-O-CH_3 + S-C_6H_5 \rightarrow [C_6H_5-O..CH_3..S-C_6H_5] \rightarrow C_6H_5-O^- + C_6H_5-S-CH_3$$

The reaction is applicable to methyl ethers other than anisole. Hexestrol and stilbestrol dimethyl ethers were both quantitatively demethylated in the presence of thiophenol and alcoholic potash after four hours heating at 200° C. Thioanisole was obtained as before and in the absence of thiophenol the yield of the phenols was very low. With stilbestrol dimethyl ether no addition of thiophenol across the double band occurred. This is in agreement with the findings of Posner (1905), who under a variety of conditions could not obtain an addition product from thiophenol and stilbene.

Although thioanisole is much more resistant to acidic and basic reagents than anisole, sodium in liquid ammonia, which rapidly and quantitatively splits thioanisole (Hughes and Thompson, 1948) has but a slow action on anisole (Birch, 1947 ; Hughes and Thompson, *loc. cit.*).

The mechanism for this reaction must therefore differ from those of the acid and basic reagents. Sodium in liquid ammonia behaves as a solution of metal cations and solvated electrons in equilibrium with metal atoms (Kraus, 1921) and consequently could be expected to react by electron addition. The ability of the sulphur atom to expand the number of electrons in its valency shell (oxygen cannot) would facilitate the formation of a transition state in the case of thioanisole.

$$C_6H_5-\overset{..}{\underset{..}{S}}-CH_3 + e^- \rightarrow [C_6H_5-\overset{...}{\underset{..}{S}}-CH_3] \rightarrow C_6H_5-S^- + CH_3.$$

With anisole the reaction is much slower, but quantitative. Thus we have found that increasing the reaction time from seven hours to fifteen hours increases the yield of phenol from 27% (Birch, *loc. cit.*) to 100%.

The formulation of the transition state by the addition of two electrons with the separation of two anions (Birch, *loc. cit.*) appears less likely than the addition of one electron followed by formation of the thiophenoxide ion and the free methyl radical. The latter would rapidly react with an ammoniated electron or an ammonia molecule to form methane and an amide ion, or methylamine and hydrogen respectively.

$$CH_3\cdot + NH_3 + e^- \rightarrow CH_4 + NH_2^-$$
$$CH_3\cdot + NH_3 \rightarrow CH_3NH_2 + \tfrac{1}{2}H_2$$

In a quantitative experiment Williams and Gebauer-Fuelnegg (1931) isolated ethane from the reaction between diethyl sulphide and sodium in liquid

ammonia and the yield of sodamide and ethane (approx. 75%) compared with the yield of sodium ethyl sulphide (95%) suggests that both these reactions may occur.

Kraus (1923) has noted the stability of aliphatic ethers to this reagent.

Experimental.

Demethylation of Thioanisole by Sodium in Pyridine.

To a stirred solution of thioanisole (12·4 g.) in refluxing dry pyridine (50 ml.) was added small pieces of sodium, the reaction being conducted in a stream of nitrogen. The solution rapidly turned purple and became progressively darker and more viscous.

After five hours the mixture was treated with aqueous pyridine to remove unreacted sodium, diluted with water and extracted with ether to remove any unchanged thioanisole.

The aqueous solution was acidified with hydrochloric acid and extracted with ether. The ether extracts after filtering to remove suspended matter were washed with water and dried over calcium chloride. Removal of the solvents by fractionation followed by distillation of the residue gave thiophenol (6·5 ml., 62%; b.p. 169–172° C.).

No thioanisole was recovered from the ether extract of the acid solution.

Under the same conditions Prey (*loc. cit.*) isolated 94% phenol from anisole.

Demethylation of Thioanisole by Aluminium Chloride.

Thioanisole (10 g.) and powdered anhydrous aluminium chloride (11 g.) were heated on a water bath for periods ranging from two to seven hours. During this time the mixture darkened in colour and sulphur containing vapours were evolved which turned lead acetate paper black.

The mixture was poured on to ice, treated with hydrochloric acid and extracted with ether. The ether layer was extracted several times with caustic soda solution and the alkaline extracts acidified and extracted with ether. After washing and drying over calcium chloride both ether extracts were carefully distilled using a fractionating column (both thiophenol and thioanisole are appreciably volatile in ether).

The yields of thiophenol were usually low and thioanisole was recovered together with other neutral products of high boiling point.

The yield of thiophenol varied from 7% to 35% (b.p. 169–172° C.) and no other substance was isolated from the alkali-soluble fraction.

The amount of thioanisole recovered varied from 75% to 30% (b.p. 194–196 °C.)

The higher boiling fractions accounted for 10–20% of the original thioanisole, but no attempts were made to identify the substances present. Some solid substances crystallised from these fractions.

Heating the mixture at 120° C. caused considerable frothing, increased the quantity of sulphur-containing vapours evolved, and lowered the yield of thiophenol.

Thioanisole and Alcoholic Potash.

Thioanisole (12·4 g.) caustic potash (8 g.) and alcohol (40 ml.) were heated in an autoclave at 230–235° C. for seven hours. The reaction mixture was poured into water and extracted with ether. The aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. After washing, drying and removal of the ether a negligible amount of oil remained.

Demethylation of Anisole by Thiophenol.

Anisole (10·8 g.), thiophenol (11 g.), caustic potash (8 g.) and alcohol (40 ml.) were heated in an autoclave at 200° C. for six hours. After cooling, water was added and the mixture extracted with ether. The ether extracts were washed with water, dried over calcium chloride and the ether fractionated off. Distillation of the residue gave only thioanisole b.p. 192–198 °C. (9·6 g.). The thioanisole was further characterised by oxidation of 2 g. in acetic acid solution with a solution of potassium permanganate (4·7 g.) in water (140 ml.). The solution was decolorised with sulphur dioxide and partially neutralised with caustic soda. The white

solid (2·2 g.) which separated was filtered off and after recrystallisation from methanol melted at 87° C. and did not depress the melting point of an authentic specimen of the sulphone of thioanisole.

The alkaline solution was acidified, extracted with ether, and the ether extracts washed and dried. Removal of the ether followed by distillation gave phenol (8 g.) b.p. 182–185 °C.

In a parallel experiment in which the thiophenol was omitted only 0·6 g. phenol (7%) was obtained.

Substitution of water (30 ml.) for the alcohol gave phenol (8 g.). When the reaction was carried out at 180° C. for six hours only 45% phenol was obtained, while at 150–170° C. for 24 hours 58% phenol was isolated.

Attempts were made to carry out the reaction at atmospheric pressure by refluxing with ethylene glycol or glycerol but after 18 hours no transfer of the methyl group had occurred. The reflux temperature in these experiments was only about 150° C.

Diphenyl ether was substituted for anisole in one experiment but no transfer occurred.

Demethylation of Hexestrol Dimethyl Ether and Stilbestrol Dimethyl Ester by Thiophenol.

The ether (1·5 g.), caustic potash (1·5 g.), thiophenol (2 ml.) and alcohol (20 ml.) were heated together in an autoclave at 200–210° C. for four hours. Water was added on cooling and the mixture extracted with ether.

The alkaline solution was acidified, boiled for several minutes to remove the volatile unchanged thiophenol and cooled.

The solid which separated was dried and recrystallised from benzene.

From hexestrol dimethyl ether was obtained hexestrol (1·35 g.) m.p. 184° C. It did not depress the melting point of an authentic specimen of hexestrol.

From stilbestrol methyl ether stilbestrol (1·35 g.) m.p. 169° C. was obtained, which was identified by mixed melting point.

The thioanisole isolated from the original ether extract was steam distilled and oxidised as before to the sulphone m.p. and mixed m.p. 87° C.

Parallel experiments in which the thiophenol was omitted gave only very small yields of the phenols.

Demethylation of Anisole by Sodium in Liquid Ammonia.

Anisole (9 g.) was added to ammonia (200 ml.) containing sodium (9 g.), with stirring during 15 minutes, in a flask surrounded by liquid ammonia contained in a Dewar flask. After standing 15 hours the ammonia was allowed to evaporate and crushed ice (100 g.) added as rapidly as was safe. The mixture was extracted with ether, the ammonia boiled from the aqueous solution, which was then acidified.

The phenol was extracted with ether (4 × 50 ml.), the solution dried, the ether removed and the phenol (7·5 g.) b.p. 181–183° C. distilled. No anisole was recovered from the ether solution.

In a similar experiment using sodium (6 g.) Birch (*loc. cit.*) obtained 27% phenol after seven hours.

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REFERENCES.

Auwers, K., and Arndt, F., 1909. *Ber. dtsch. chem. Ges.*, **42**, 537.
Baddeley, G., 1944. *J. chem. Soc.*, 330.
Bagster, L. S., 1911. *J. chem. Soc.*, **99**, 1218.
Birch, A. J., 1947. *J. chem. Soc.*, 102.
Fehnel, E. A., and Carmack, M., 1949. *J. Amer. chem. Soc.*, **71**, 2890.

Gilman, H., and Webb, F. J., 1940. *J. Amer. chem. Soc.*, **62**, 987.

Harnish, D. P., and Tarbell, D. S., 1948. *J. Amer. chem. Soc.*, **70**, 4123.

Hughes, G. K., and Thompson, E. O. P., 1948. THIS JOURNAL, **82**. In press.

Jablczynska-Jedrzejewska, H., and Groyecka, J., 1937. *Roczniki Chem.*, **17**, 392 ; *Chem. Abstr.*, **32**, 1546.

Kraus, C. A., 1921. *J. Amer. chem. Soc.*, **43**, 764.

Kraus, C. A., and White, G. F., 1923. *J. Amer. chem. Soc.*, **45**, 770.

Lee, S. W., and Dougherty, G., 1939. *J. org. Chem.*, **4**, 48.

Posner, T., 1905. *Ber. dtsch. chem. Ges.*, **42**, 537.

Prey, V., 1943. *Ber. dtsch. chem. Ges.*, **76B**, 156.

Remick, A. E., 1942. *J. org. Chem.*, **7**, 534.

Stoemer, R., and Kahlert, B., 1901. *Ber. dtsch. chem. Ges.*, **34**, 1812.

Williams, F. E., and Gebauer-Fuelnegg, E., 1931. *J. Amer. chem. Soc.*, **53**, 352.

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ACTION OF PHOTOCHEMICALLY PRODUCED RADICALS ON ACETYLENE.

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INTRODUCTION.

The photodecomposition of zinc diethyl has been studied by Moore and Taylor (1940), who postulated the following reactions:

$$Zn(C_2H_5)_2 \xrightarrow{h\nu} C_2H_5 + ZnC_2H_5 \quad \ldots\ldots\ldots \text{(1)}$$

$$C_2H_5 + Zn(C_2H_5)_2 \longrightarrow C_2H_6 + C_2H_4 + ZnC_2H_5 \quad \ldots\ldots \text{(2)}$$

together, presumably, with

$$ZnC_2H_5 \longrightarrow Zn + C_2H_5 \quad \ldots\ldots\ldots\ldots \text{(3)}$$

Evidence presented in this paper supports this mechanism.

It is to be noted that reaction (1) involves the liberation of free ethyl radicals from the zinc diethyl molecule, a process which must take place within one vibration period as there is a continuum in the ultra-violet absorption spectrum of zinc diethyl below 280 mμ (Thompson (1935) and Thompson and Linnett (1936)).

Now there is evidence that gaseous acetylene can be polymerised even at room temperature by the action of free radicals, e.g. by methyl radicals formed in the photolysis of acetone (Taylor and Jungers (1937)).

$$CH_3COCH_3 \longrightarrow CH_3 + CH_3CO$$

this phenomenon has been observed in the course of these experiments also.

Thus there was good reason to expect that the photolysis of zinc diethyl in the vapour phase would induce polymerisation of gaseous acetylene. The study of this reaction is now reported.

EXPERIMENTAL.

The apparatus is illustrated in Fig. 1.

The *lamp*, shown at left in Fig. 1, was a high-pressure type, the discharge taking place in an inverted U-tube. The 253·7 line was reversed.

The *effect of light on acetylene* itself was one possible complication. The photopolymerisation of this substance has been studied by Lind and Livingstone (1930), who found a quantum yield of nine at 215 mμ. Wave-lengths much higher than this are not absorbed. Therefore, using the full light of our quartz mercury lamp, which had only a slight output in the active range, only a slight direct photopolymerisation was to be expected. Tests showed that this was negligible for our purposes.

The *pressure gauge* was an ordinary mercury manometer.

The presence of mercury vapour did not affect the reaction because of the absence of the 253·7 mμ line. A *trap* included in the line served to hold the distilled zinc diethyl before volatilisation into the reaction vessel. A *Töpler*

pump was used to collect product gases. The *zinc diethyl* was prepared and purified according to the method of " Organic Syntheses ". It was stored in the dark and separated from the rest of the apparatus by two stopcocks. *Acetylene* was obtained from a cylinder and passed through sodium bisulphite and sodium hydroxide solutions and a dehydrating chain.   It was also frozen and revolatilised three times, with appropriate evacuation of the last fraction each time, before being stored in a bulb.   *Acetone* was purified by the method of Weissberger and Proskauer (1935), distilled into the trap, and then admitted to the reaction vessel.   During a run the reaction vessel was shut off from all but the pressure gauge.   Room *temperature* conditions were held by a stream of water over the outside of the reaction vessel.   A *zinc film* appeared on the inside wall nearest
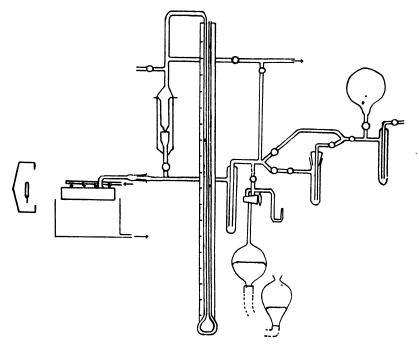
Fig. 1.

the light when zinc diethyl was used.   This was estimated at the end of a run as follows : The zinc was dissolved in dilute sulphuric acid and the volume made up to 100 ml.   Ten millilitres of this were made just alkaline with dilute ammonia, extracted with dithizone solution in redistilled chloroform.   The chloroform extract was washed with ammonia and made up to 25 ml.   This red solution was compared in a " Spekker " photoelectric colorimeter with similar preparations made from standard zinc sulphate solutions.

RESULTS.

(1) A film of polymer appeared on the inside of the reaction vessel whenever zinc diethyl or acetone was present with acetylene.   The polymer was light-brown in colour and resembled cuprene.   It was stable to heat in a vacuum. It was insoluble in ordinary organic solvents and also in concentrated nitric acid.   Examination with a polarising microscope showed it to be slightly birefringent, but X-ray photographs both of a flake and of a powder made from it showed no sign of a crystal structure.

(2) Irradiation of an acetone-acetylene mixture gave results shown in Table I.

(3) Irradiation of zinc diethyl, acetylene and mixtures of the two gave results which are summarised in Table II.

In the table, results in lines 2, 3, 4, 5, 8 and 10 are all based upon independent experimental measurement. Figures in lines 6, 7 and 11 are deduced from the others. Figures in line 10 are calculated from the amount of metallic zinc deposited and found by analysis.

TABLE I.
Acetone–Acetylene.
Time of irradiation : 1130 mins. Temperature : 22° C.

	Initial Pressure. (Mm.)	Final Pressure. (Mm.)
Acetylene	137	—
Acetone	188	—
Carbon monoxide ..	—	8·3 (by analysis)
Total	325	318

TABLE II.
Zinc Diethyl, Acetylene.
Temperature : 22° C. ±2. Pressures in mm. mercury.

1	Run	11	13	14	15	16	17
2	Time (mins.)	117	135	40	82	81	153
3	$Zn(C_2H_5)_2$, initial	19	0	20	20	16	14·5
4	C_2H_2, initial	0	282	215·5	142	0	325
5	Total, final..	21·5	281	239	163	·19	342
6	$Zn(C_2H_5)_2 + C_2H_2$, final ..	—	—	206	142	—	318
7	$Zn(C_2H_5)_2$, final ..	—	—	—	16·8	19	10
8	C_2H_2, final	—	—	—	125·5	—	308
9	Product gases	—	—	44	21	5·7	24
10	Decrease in $Zn(C_2H_5)_2$ ..	—	—	—	3·2	2·7	4·5
11	Decrease in C_2H_2	—	—	—	16·5	—	17

Notes.
Run 12 discarded as analysis revealed acetylene to be impure.
Runs 1–10 were made with an insufficiently accurate manometer and were discarded.

DISCUSSION OF RESULTS.

(1) The efficiency of the free radicals from acetone in polymerising acetylene may be estimated as follows :

One molecule of carbon monoxide is formed from one molecule of acetone so that a measure of the acetone decomposed is possible. After allowing for the carbon monoxide present in the final mixture, the decrease in total pressure which was observed is a direct measure of the acetylene polymerised, since one molecule of acetone gives rise to one molecule of ethane besides the carbon monoxide. Biacetyl is not formed in the presence of a foreign gas (Iredale and Lyons (1944)).

Let $p_{0,f}$ denote the original, final pressure, and

p_{CO} ,, ,, carbon monoxide pressure.

Then number of molecules of acetylene polymerised for each free radical

$$\text{produced} = \frac{p_0 - p_t + p_{CO}}{p_{CO}}$$

$$= \frac{325 - 318 + 8}{8}$$

$$= 1 \cdot 9 \text{ molecules/radical.}$$

This agrees with the results of Taylor and Jungers (1937).

(2) The photolysis of zinc diethyl is known to give no butane at room temperatures, but only ethylene and ethane, i.e. one molecule of zinc diethyl gives two molecules of products (Moore and Taylor (1940)).

From Table II, run 16, it is seen that one molecule of zinc diethyl does give $2 \cdot 1$ moles of products, and so the earlier work is confirmed.

(3) In the runs where acetylene was present with the zinc diethyl, the results indicate the formation of vapour products other than from the zinc diethyl, e.g. in run 15 there were $6 \cdot 7$ moles of products for one mole of zinc diethyl used, and in run 17, $5 \cdot 3$ moles of products. The gaseous products were in every case completely condensable with liquid air, indicating that neither hydrogen nor methane was present.

As the only possible source of gaseous products apart from the zinc diethyl was the acetylene itself, it is concluded that the reaction produces from the acetylene (a) a volatile compound as well as (b) a solid polymer.

(4) The ethyl radical polymerisation efficiency may be calculated by saying that :

Number of radicals produced $= 2 \times$ number of molecules of zinc diethyl decomposed.

The results give $2 \cdot 5$ molecules polymerised/radical for run 15, · and $1 \cdot 9$ molecules polymerised/radical for run 17.

These figures may be compared with $1 \cdot 9$ molecules/methyl radical (see above) for acetone-acetylene, a figure obtained by a totally different method. Thus it may be said that methyl and ethyl radicals are of about equal efficiency in polymerising acetylene.

(5) The percentage of ethyl radicals efficient in producing polymerisation may be calculated assuming a mean number of C_2 units in the polymer.

For three units in the polymer, 75 % of the radicals are effective polymerising agents, for four units 55 % and for six, 37 %. So it is seen that about one in every two radicals initiates a chain.

SUMMARY.

(1) Zinc diethyl photolysis involves free radicals and the previously postulated mechanism is supported.

(2) Acetylene is polymerised by methyl and ethyl radicals with about equal efficiency.

(3) The products of the polymerisation are (a) a volatile substance, and (b) a non-crystalline solid.

(4) $2 \cdot 2$ molecules of acetylene polymerise for each radical produced.

(5) One in every two radicals initiates a chain.

REFERENCES.

Iredale, T., and Lyons, L. E., 1944. *J. Chem. Soc.*, 688.
Lind, S. C., and Livingston, R., 1930. *J. Amer. Chem. Soc.*, **52**, 443.
Moore, W. J., and Taylor, H. S., 1940. *J. Chem. Phys.*, **8**, 396.
Taylor, A. S., and Jungers, J. C., 1937. *Trans. Far. Soc.*, **33**, 1353.
Thompson, H. W., 1935. *Proc. Roy. Soc. (Lond.)*, A, **150**, 603.
Thompson, H. W., and Linnett, J. W., 1936. *Ibid.*, A, **156**, 108.
Weissberger, A., and Proskauer, E., 1935. " Organic Solvents." (Oxford.)

A FURTHER CONTRIBUTION TO THE GEOLOGY OF THE GOULBURN DISTRICT, N.S.W.

By G. F. K. NAYLOR, M.A., M.Sc., Dip. Ed.

PART I. EVIDENCE OF A MAJOR FOLD-STRUCTURE IN THE PALÆOZOIC ROCKS TO THE EAST OF GOULBURN.

In a paper published in this journal in 1935 (Naylor, 1935) the writer expressed the opinion that certain observed relationships between Silurian and Ordovician strata near Bungonia could best be explained by the assumption of an overfolded structure.
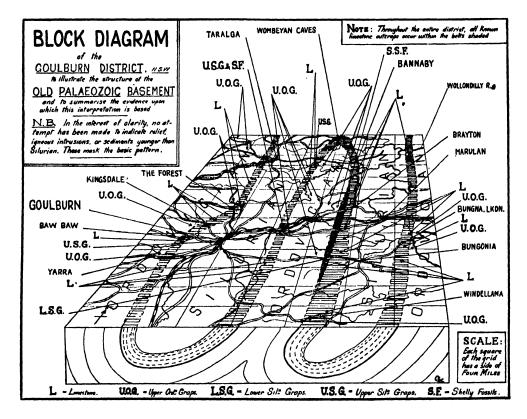
This seemed to afford the best suggestion to account for the fact that rocks with a definite Upper Ordovician graptolite fauna overlie (in the field) other strata with equally definite Lower Silurian graptolites. The evidence for the fold structure was then admittedly incomplete ; but shortly after the publication of the paper mentioned additional field work enabled many of the gaps to be filled in. The writer was preparing a further communication on this matter in 1939, but was interrupted by the war. No more field work was possible until 1945, and this tended to confirm the evidence for the fold structure, while bringing to light certain unexpected facts which render necessary a complete review of the Palæozoic sequence near Goulburn itself. It was the intention of the writer to carry out the field work necessary to attempt this review, and to publish the additional evidence for the fold structure at the same time. Since his appointment to the staff of the University of Queensland in 1946 no opportunity to renew field work at Goulburn has occurred, and may not do so for some time. Hence this opportunity is being taken to present the data at present available, for the benefit of other workers in adjoining areas. A brief mention will also be made of the evidence which appears to preclude the acceptance of the Upper Devonian age that has been traditionally assigned to the rocks in the immediate vicinity of Goulburn.

Summary of Observations Previously Recorded.

On the road section between Bungonia and Goulburn were noted rocks of Upper Ordovician age. These dipped steeply to the west and apparently overlay strata containing a Lower Silurian graptolite fauna, also dipping to the west. These in turn appeared to overlie a series of slates and quartzites including isolated patches of limestone, which were assumed, in the absence of evidence to the contrary, to be of Upper Silurian age. There was thus an apparent inversion of these three series, suggesting that they occupied the underlying limb of a great anticlinal fold, overturned towards the east. It was assumed that the Upper Silurian Series east of Bungonia represented the eastern limb of an adjacent syncline. It was further inferred from the presence of Silurian graptolites on the Marulan-Goulburn road section, that Silurian rocks were present on the western limb of the anticline, adjacent to the western boundary of the Ordovician belt. The assumed structure was indicated in a sketch section published along with the paper.

Additional Evidence from Bungonia-Goulburn Section.

(*a*) In a paper written in 1936, Garretty (1936), while agreeing generally with the structure offered above, suggested that the limestones in portions 18 and 46 ph. Jerrara, might be of Devonian rather than Silurian age, as previously assumed by the present writer. A more recent examination, however, has revealed that a bed of limestone, not outcropping at the surface, has been met in a shaft sunk a little to the north of the outcrop in portion 18. Amongst the blocks of limestone which had unquestionably been removed from the shaft and hence may be regarded as being *in situ*, were found good specimens of *Pentamerus knighti*, supporting the assumption of an Upper Silurian age for this limestone belt.

BLOCK DIAGRAM
of the
GOULBURN DISTRICT. *N.S.W*
to illustrate the structure of the
OLD PALAEOZOIC BASEMENT
and to summarise the evidence upon which this interpretation is based

N.B. *In the interest of clarity, no attempt has been made to indicate relief, igneous intrusions, or sediments younger than Silurian. These mask the basic pattern.*

NOTE: *Throughout the entire district, all known limestone outcrops occur within the belts shaded*

L - *Limestone.*   U.O.G. - *Upper Ord: Graps.*   L.S.G. - *Lower Sil: Graps.*   U.S.G. - *Upper Sil: Graps.*   S.F. - *Shelly Fossils.*

More convincing evidence of the pre-Devonian age of the limestones lies in the fact that they are metamorphosed by the Marulan batholith, while the known Devonian lies upon its eroded surface (Naylor, 1939).

(*b*) Thanks to information supplied by a local resident, Mr. I. Frost, limestone has been located and examined by the writer in two adjacent localities to the west of the Ordovician belt along the course of McKellar's Creek, about six miles east of Goulburn. The two outcrops of limestone occurring here do not appear to have been recorded by Carne and Jones in their survey. They are small in extent and of no economic significance. Both outcrops are marmorised by the contact effects of the adjacent porphyritic rocks, but contain numerous fossils, mainly tabulate and rugose corals, an assemblage corresponding to that of the Silurian limestones elsewhere. *Favosites* and *Heliolites* are recognisable generically but the species are indeterminate.

(c) A series of relatively soft light-bluish-grey clay-stones are met immediately to the west of the limestones on the eastern side of the Ordovician belt. From this, however, they are separated by the Lower Silurian shales of the Jerrara Beds, and hence they must be assigned to the Silurian group. Whether they should be classed as Upper or Lower Silurian is a matter of doubt, since they themselves appear to contain no fossils. However, what is presumably the same horizon has been located a little to the east of the McKellar's Creek limestone, adding to the symmetry of the distribution of the strata, and lending support to the assumption of an anticlinal fold. Additional confirmatory evidence in favour of this interpretation is offered by the distribution of the quartzitic horizon of the Silurian series.

(d) The Upper Ordovician rocks themselves show a similar tendency towards symmetrical distribution of characteristic horizons, while a zone towards the central part of the belt shows evidence of great compressive stresses such as might be expected to occur along the axis of a fold some distance below the original surface.

The corresponding rock zones on either side of this supposed axis tend to be wider to the west than to the east. However, this would appear to agree well with the conception of an over-fold in which it is reasonable to expect the upper (here western) limb to be thickened by compression, while the thickness of the lower (eastern) limb would be reduced by tension.

Evidence from the Marulan-Goulburn Section.

Proceeding west from Marulan the igneous rock is found to extend for about a mile and a half beyond the Bungonia turn-off, after which one meets relatively gently dipping quartzites and sandy shales (dip W. at 30°–40°). These may be of Upper Devonian age and consequently not immediately connected with the problem of the Ordovician and Silurian folding. However, this should not be too readily assumed. Further on, the dip of the strata is found to be steeper, reaching the 50°–80° range characteristic of the older Palæozoic rocks. Lithologically the rocks here consist of quartzites with thin interbedded bands of slate and claystone, the colour and texture of both being characteristic of those associated with the Silurian elsewhere. Just before reaching Shelley's Flat, a thick series of soft bluish-grey claystones, almost devoid of quartzites, occurs. On the eastern edge of these shales, just opposite the residence of Mr. Henderson, to whom the writer is indebted for the information, is a very small outcrop of what is probably a larger underlying mass of limestone. The small amount of limestone that is exposed is quite fossiliferous, the types including tabulate and rugose corals, not well enough preserved for specific identification.

Another small outcrop of limestone, which more closely approaches a travertine, occurs about a mile to the south, but is probably of secondary origin and hence of little immediate structural significance.

Occupying the " Flat " itself, and largely masked by alluvium, is a series of slates which seem to correspond with the Jerrara Beds, though graptolites have not been found in them in this locality. (It should be pointed out that the extent of the Jerrara series has been investigated further since the writer's earlier paper, and is now known to be at least four miles along the strike, having been traced on either side of the Bungonia-Goulburn road as far south as Bungonia Creek and as far north as Jerrara Creek. A continuation of this line would intersect the Hume Highway very close to Shelley's Flat, and pass northward a little to the west of Brayton.)

From the western edge of the Flat almost to the Carrick turn-off, a distance of about five miles, one passes over graptolite-bearing rocks of Upper Ordovician age. These are lithologically distinct from the Silurian types. Well cleaved

bluish-grey slates, quartz schists, and blue cherts predominate. The slates are much harder than those of the Silurian, especially of the Upper Silurian.

Graptolites are plentiful towards the margins, though occasionally their collection is rendered difficult by the development of cross-cleavage. A small collection taken from the Carrick Road on the western margin was submitted some years ago to Dr. D. E. Thomas, who identified the forms as belonging to an extreme Upper Ordovician horizon.

A much more extensive collection has now been made by the author from cuttings in more recently constructed deviations in the Hume Highway. Two horizons in which graptolites are particularly abundant occur on the western and eastern margins of the Ordovician belt. The graptolites in these two localities are quite well preserved, and the similarity of the assemblages shown below would appear to suggest beyond reasonable doubt that the same horizon is represented in both cases. The extreme Upper Ordovician age of this horizon is also indicated.

(a) *Forms occurring in the Western Locality.*

Dicellograptus sp.
Diplograptus truncatus.
Diplograptus quadrimucronatus var. *spingerus.*

Climacograptus cf. *rectangularis.*
Climacograptus sp.
Leptograptus cf. *capillaris.*
Diplograptus cf. *calcaratus.*
Diplograptus calcaratus var. *tenuicornis.*

(b) *Forms occurring in the Eastern Locality.*

Climacograptus rectangularis.
Climacograptus supernus.
Climacograptus sp. (other than above)
Diplograptus sp.
Retiograptus cf. *pulcherrimus.*
Dicellograptus pumilus.
Dicellograptus cf. *forchammeri.*

About 200 yards east of the Carrick Road Junction, the Ordovician strata give place to soft greyish-blue shales containing *Pentamerus knighti* and other shelly fossils, as well as recognisable *M. bohemicus.* Another hundred yards to the west are finely banded bluish-grey shales containing Upper Silurian graptolite forms (Naylor, 1935a). These shales, with interbedded quartzite, can be traced onward as far as Boxer's Creek, where they are terminated by a porphyritic intrusion about half a mile in width. Thereafter the slates continue to the foot of Governor's Hill, where there is no clear boundary between these and the arenaceous rocks that have hitherto been accepted as Upper Devonian. It can be seen from this description that the main features of the section along the Hume Highway are very similar to those of the section along the Bungonia-Goulburn road, a distance of four to six miles further south.

Evidence from an East-West Section through Brayton.

The sedimentary rocks to the north and west of Brayton are separated from those just described by a westward projection of the Marulan batholith, but corresponding types are found and there is no doubt of their original continuity with those of the areas just described. The relation between the Silurian and Ordovician strata near Brayton which puzzled the writer for many years becomes simplified in the light of the folding deduced from observations further south.

Adjoining the porphyritic complex near Brayton Cross-roads is an outcrop of marmorised limestone, to the west of which are hornfelses and metamorphosed tuffs, together with interbedded flows of lamprophyre. This region appears to have been a volcanic centre in Silurian times, but most of the metamorphism is

probably due to the proximity of the batholith. What may be called the " volcanic " series can be traced westward for about a mile and is succeeded first by quartzites then by a thick series of slates with very little quartzite. These extend for fully half a mile, until finally there is exposed in a creek bed a highly silicified rock containing numerous Silurian shelly fossils, in which the genus *Atrypa* predominates. (These were identified as definitely Silurian by the late Mr. Chapman.) Fifty yards beyond this point the lithology changes and the characteristic hard, cleaved, bluish-grey slates and cherts of the Ordovician series outcrop.

All the rocks here are dipping to the westward, so that the Silurian appears to underlie the Ordovician, an impression which is greatly strengthened by the fact that the fossiliferous bands on the edge of the Silurian outcrop in the creek bed, while Ordovician graptolites may be collected high above them on the hillsides.

The exact age of the Silurian rocks here is doubtful. It may be assumed with reasonable safety that the Brayton limestone is Upper Silurian, since this age has been proved for most of the limestones in this district. It is highly marmorised and fossils are very scarce. The writer is inclined to the opinion, based on lithological similarity, that the western portion of the slates corresponds to the Jerrara series and hence is of Lower Silurian age. This would imply that the fossiliferous beds adjacent to the Ordovician are also Lower Silurian—an assumption which the fossils themselves do not appear to either confirm or deny. While undoubtedly Silurian types, their exact horizon is so far indeterminate.

The Ordovician beds nearest the Silurian contain fairly well preserved graptolites, and would appear to represent the uppermost part of the Upper Ordovician system. The following forms have been collected :

Climacograptus bicornis.
Diplograptus quadrimucronatus.
Dicellograptus complanatus.

West of Brayton the Ordovician belt extends for about four miles to the foot of the main Cookbundoon Range, where it is unconformably overlain by the marine sediments of the Upper Devonian. Graptolites are fairly numerous throughout this region of Ordovician rocks, but there are certain marked changes in the distribution of the forms which have a distinct bearing on the present problem.

As has been pointed out, the eastern margin appears to be of very late Ordovician age. About two miles further west, however, near the Greenwich Park-Towrang Road, occur numerous graptolites of a distinctive and diminutive nature which were regarded by Dr. Thomas as being representative of the lowest part of the Upper Ordovician, and the writer's own observations seem to point to the same conclusion. The list of forms identified by Dr. Thomas are as follows :

Dicellograptus sextans.
Cryptograptus tricornis.
Dicellograptus divaricatus var. *augustus* (nov.).
cf. *Leptograptus.*
Diplograptus sp.

Further west again the fauna appear to belong to a higher zone :

Dicellograptus elegans.
Climacograptus cf. *caudatus.*
Dicranograptus hians var. *apertus.*

For these identifications the writer is also indebted to Dr. Thomas.

In this line of section one cannot inspect the western junction between Ordovician and Silurian series since it is overlain by the Devonian strata. However, in the same line, beyond the Cookbundoon Range, the Silurian limestones of The Forest are situated a little to the east of another graphite-bearing Ordovician belt.

<div style="text-align:center">Evidence from the Section near Kerrawary Creek and the
Cookbundoon River.</div>

The information so far available concerning this section is not very detailed but is significant when considered in conjunction with the other sections just described.

North of Big Hill, on the southern bank of the Cookbundoon River, about two miles west of the Swallow-tail Pass, there occurs an isolated outcrop of marmorised limestone extending discontinuously for about a quarter of a mile along the western margin of the igneous intrusion that occupies so much of the country in that vicinity. No fossils other than crinoids have survived the metamorphism to which this limestone has been subjected, but its alignment corresponds to that of the Bungonia-Brayton limestone belt, and supports the assumption of its Silurian age. Further west, near the junction of the River with Kerrawary Creek, occur graptolites which are definitely Upper Ordovician types, though an exact list of forms is not available. A collection made by the writer from the western portion of this belt between Kerrawary Creek and the Bannaby-Taralga road includes the following types :

> *Diplograptus calcaratus.*
> *Dicellograptus* cf. *complanatus.*
> *Dicellograptus complanatus* var. *ornatus.*
> *Dicranograptus clingani.*

Still further westward near the junction of Kerrawary Creek and Cowhorn Gully, there is a prominent outcrop of fossiliferous Upper Silurian limestone with interbedded shales containing *Monograptus*. These have already been noted by the writer (Naylor, 1937). West of Taralga Upper Ordovician graptolites have been collected at numerous localities in the vicinity of Goldspie and Yalbraith, and at Bumaroo Ford.

<div style="text-align:center">Summary of Evidence.</div>

It is readily admitted that the data available in any single one of these sections is, for various reasons, incomplete ; but considering the evidence as a whole the conclusion that there is a major overfolded anticlinal structure in the Ordovician and Silurian rocks appears to be inescapable. What is lacking in one section is supplied from a parallel one. Thus the absence of graptolites on the western part of the Bungonia-Goulburn Section is compensated by their abundance on the corresponding part of the Marulan-Goulburn Section, where the boundary between Ordovician and Silurian strata is well defined. Similarly the absence of Upper Silurian limestone from this part of the latter section is offset by the occurrence in McKellar's Creek. The lamprophyres and breccias characteristic of the Silurian series at Brayton may or may not occur beneath the Devonian strata to the west of the Ordovician belt, but they certainly have a counterpart in the western Silurian belt between the Bungonia-Goulburn and Marulan-Goulburn roads.

<div style="text-align:center">Stratigraphical Implications.</div>

Certain inferences concerning the sequence and relationship of the older Palæozoic rocks may be drawn from the foregoing discussion. In the first place it would appear that the structures present are fundamentally simpler than had previously been supposed. An anticline rather than an anticlinorium

is suggested. It is true that much local folding may be observed throughout the area but this has never been traced for any appreciable distance. Moreover such folding appears to be confined to the more argillaceous sediments and may readily be attributed to " drag folding " caused by differential movement of more competent arenaceous beds on either side. These latter, as far as the writer is aware, exhibit only simple though steep dips.

If one accepts the existence of a huge and relatively simple anticline, to which the existing evidence tends to point, the folding of both Upper Ordovician and Silurian strata would appear to have resulted from the one movement. In other words the two series seem to be substantially conformable throughout. This view is supported by field evidence, since not only do both series appear to have suffered the same degree of folding, but where the junction between them can be located, no significant angular variation in the strike or dip has been observed.

Woolnough (1909), in the original paper on the Tallong-Marulan district, described an unconformity beneath the Upper Silurian limestone at Marulan, and the position of this structure has since been located exactly by Dr. G. D. Osborne. Geological opinion concerning the relations between Ordovician and Silurian in N.S.W. appears to have been considerably influenced by this occurrence, but the writer feels that it would be inadvisable to attach too much stratigraphical or structural significance to the angular nature of the exposed junction between the Marulan limestone and the underlying slates. In this locality the limestone is hundreds of feet in thickness and must have offered great resistance during the folding processes, with an almost inevitable disturbance of the original relationship between it and the adjoining less competent argillaceous beds. Moreover, the beds immediately below the limestone have never been proved to be of Ordovician age. This has merely been inferred from the assumption of unconformable relations. The writer, who has examined this locality, considers that the slates present the lithological characteristics suggestive of Silurian rather than Ordovician types, and it is significant that in no other locality have the limestones been shown to be the basal member of the Silurian series. Finally, angular discordance may be observed from Bungonia Lookdown between the base of the Upper Belt of limestone and the (presumably argillaceous) rocks which separate it from the Lower Belt.

In short, the bulk of the evidence at present available from the Bungonia-Goulburn district seems to indicate the absence of any appreciable epi-Ordovician orogeny, though the transition in many places from Upper Ordovician to Upper Silurian strata certainly implies a discontinuity of sedimentation.

Epi-Silurian folding, however, must have taken place on a grand scale, affecting both Upper Ordovician and Silurian strata, producing between Marulan and Goulburn a huge anticline which was overturned to the east. During this folding the Ordovician rocks, being more deeply buried, suffered a greater degree of dynamic metamorphism than the overlying Silurian strata. It is suggested that this accounts for the fact that the former exhibit a greater degree of recrystallisation and a more disturbed character than the latter, though the general dips of both series are, equally steep.

An exception to the steep dips of the Silurian strata occurs in the immediate vicinity of Goulburn itself, where the competent nature of a large mass of quartzite appears to have exerted considerable resistance to the folding and resulted in shallower local dips (see Part II).

PART II.   EVIDENCE CONCERNING THE AGE OF THE SEDIMENTARY
ROCKS AT GOULBURN.

Those responsible for compiling the State Geological Map must have had some reason for assigning a Devonian age to a large area of country surrounding

the City of Goulburn and extending eastwards towards the Shoalhaven River. In view of the fact that the great bulk of this region has now been shown conclusively to be either Ordovician or Silurian, it is difficult to be certain what the basis of the earlier classification was. As far as the writer is aware from enquiries of the personnel of the Geological Survey, the provisional assignment of a Devonian age to these rocks was largely influenced by the collection of *Lepidodendron australe* and some marine fossils with strong Lambian affinities on the summit of the Cookbundoon Range. No doubt the lithological characters of the white quartzite of the Memorial Hill and the associated conglomerates and red beds further suggested that these rocks should be regarded as Devonian.

This view was absorbed by the writer as a student and never seriously questioned by him (or as far as he is aware, by anyone else) until quite recently. However, a careful examination of the actual state of knowledge on this matter has served to convince the writer that the following are the facts of the case :

(a) The finding of *Lepidodendron australe* and the Lambian marine assemblage on the Cookbundoon Range at several localities has been confirmed personally by the writer's own collection of these forms at points along the whole length of the Cookbundoon Range from Narrangaril Trig. Station to the vicinity of Bannaby.

(b) Similar marine Upper Devonian fossils occur in arenaceous beds along the course of Bungonia Creek, near Bungonia. (These are the beds which have been shown by the writer (Naylor, 1939) to lie upon the eroded surface of the Marulan batholith.)

(c) No Devonian fossils have been found closer to Goulburn than those at Narrangaril Trig.—about five or six miles N.E. of the centre of the city.

(d) There is no record of any collection of recognisable fossils from any of the quartzites, conglomerates or shales of the Memorial Hill, Governor's Hill or the immediate surroundings. The writer has literally spent weeks in a fruitless search for fossils in these rocks.

(e) The continuity which has always been assumed to exist between the Memorial Hill quartzites and those of the Cookbundoon Range is by no means evident when one inspects aerial photographs of this region. The strike of the undoubted Upper Devonian (fossiliferous) beds of the Narrangaril locality is seen to sweep round to the westward without crossing the Wollondilly River or the main railway line, assuming a direction almost at right angles to the trend of the great whale-back of quartzite that extends for a couple of miles N.N.E. of the big Railway Department quarry at North Goulburn. Large alluvial flats at the bend of the river obscure the actual relationships of these two rock masses at what would appear to be their point of junction.

(f) The discontinuity suggested by the aerial photographs is supported by field inspection of the critical area on the ground. Discontinuity can hardly be proved, but seems to constitute a more reasonable assumption than continuity. Whether there is or is not continuity (i.e. with or without conformity) the field evidence leaves no doubt that the Narrangaril beds would certainly overlie the Goulburn quartzites if they did all form part of the one series.

(g) The quartzites outcropping in the North Goulburn Railway quarry are associated with bands of something akin to a quartz schist, in which carbonaceous fragments suggestive of organic remains are here and there abundant. The late Dr. F. A. Singleton, on viewing specimens of these, unhesitatingly proclaimed them to be graptolitic. However,

the writer himself is not prepared to make this claim, as he has been unable to distinguish any signs of graptolitic structure to his own satisfaction.   Nevertheless, he has collected exactly similar specimens from the point of view of lithology and carbonaceous content at points north of Murray's Flats, where the sediments underlie the Narrangaril beds, and appear to be unconformably separated from them.

(h) A careful examination, which the writer has been enabled to carry out many times, of an east-west section from the Memorial Hill through the City of Goulburn to and beyond the water storage tanks on the top of the hill to the west of the city, leads to the conclusion that the Memorial quartzite underlies the shaly and sandy beds on which the city itself is mainly built.   These are folded into a syncline whose nearly meridional axis lies slightly west of the city.

(i) In May 1945 the writer was fortunate enough to locate a horizon within this syncline where *Monograptus bohemicus* was abundant and easily recognisable.

CONCLUSION.

This would appear to justify the assumption of an Upper Silurian age for the beds of the Goulburn Syncline.

While the above facts do not provide positive evidence of the exact age of the Memorial Quartzite and its associated conglomerates, it seems unlikely that they are younger than Upper Silurian.   The dips of these rocks would appear to be shallow in contrast with those of the Silurian elsewhere in the Goulburn district—a fact which has no doubt contributed to the general impression of their Devonian age.   However, the beds in which *Monograptus* was collected are themselves dipping gently (E. 20° S. at 30°) and in any case the Yass district provides an example of a region where the folding of the Silurian strata has been comparatively gentle over a localised area.

REFERENCES.

Garretty, M. D., 1936.   Geological Notes on the Country between the Yass and Shoalhaven Rivers.   THIS JOURNAL, **70**, 364.

Naylor, G. F. K., 1935.   Note on the Geology of the Goulburn District, with Special Reference to Palæozoic Stratigraphy.   THIS JOURNAL, **69**, 75.

———————— 1935b.   The Palæozoic Sediments near Bungonia : Their Field Relations and Graptolite Fauna.   THIS JOURNAL, **69**, 123.

———————— 1939.   The Age of the Marulan Batholith.   THIS JOURNAL, **73**, 82.

———————— 1937.   Preliminary Note on the Occurrence of Palæozoic Strata near Taralga, N.S.W.   THIS JOURNAL, **71**, 45.

Woolnough, W. G., 1909.   The General Geology of Marulan and Tallong, N.S.W.   *Proc. Linn. Soc. N.S.W.*, **34**, 782.

THE KUTTUNG VULCANICITY OF THE HUNTER–KARUAH DISTRICT, WITH SPECIAL REFERENCE TO THE OCCURRENCE OF IGNIMBRITES.

By G. D. OSBORNE, D.Sc., Ph.D.

CONTENTS.

INTRODUCTION.

The Kuttung Series in N.S.W. occupies the time interval from the top of the Tournaisian (mid-Lower Carboniferous) to the base of the Permian System. Thus it is to be regarded as the upper part of the Carboniferous in this State, although the flora of the Series suggests a correlation with the Middle Carboniferous of the Northern Hemisphere rather than with the Upper Carboniferous (Walkom, 1919).

This Series was described from the Lower Hunter District and named by T. W. E. David and Sussmilch (1919), and was assumed to succeed the Lower Carboniferous Burindi Series. This region thus became known as the type-area, and later was intensively studied by Osborne (1922–1925), but subsequent researches in other districts by W. R. Browne and S. W. Carey (see 1938, p. 591) established the contemporaneity of the Lower Kuttung Series (the Basal and Volcanic Stages of Osborne) and the Upper Burindi, both of these stratigraphical units being approximately synchronous with the Viséan of Europe.

In all places in N.S.W. where the terrestrial Kuttung Series has been studied a lower dominantly volcanic section and an upper dominantly glacial section have been recognised, although evidences of vulcanism over a wide area during the Glacial Stage are forthcoming in the development of the Paterson type of toscanite-dellenite lavas, and many pyroclastic units interbedded with glacial sediments. Nevertheless, the period of the Lower Kuttung witnessed an intensive vulcanicity probably greater than that of any other Palæozoic epoch. This was succeeded, after a lapse of time and some diastrophic activity, by relatively quiet conditions with extensive clastic sedimentation in the Lower Glacial Stage of the Upper Kuttung. The Upper Glacial Stage was marked by local volcanic activity in a number of places, as at Stroud, Raymond Terrace District, Pokolbin and Stanhope, but elsewhere was characterised by accumulation of glacial sediments, with an absence of lava and true pyroclastic deposits.

In earlier papers upon the Lower Hunter and Karuah Districts, the writer dealt in detail with the stratigraphy and petrography, but refrained from

discussing critically the broader aspects and petrogenetic significance of the lava-sequences, and the mode of development and/or accumulation of the pyroclastic rocks. This policy was followed because of the imperfect state of our knowledge of the problems involved.

The present paper deals mainly with the great volcanic succession of the Lower Kuttung, although the Upper Kuttung will be considered to some extent.

The aims of the paper may be stated to be as follows :

(a) To review the salient facts about the vulcanicity in the light of informa- tion from researches upon the *nuée ardente* type of eruption.

(b) To describe the field occurrence and widespread distribution of the ignimbrites in the succession.

(c) To relate the time of the ignimbrite-development to the general frame- work sequence of the Volcanic Stage.

(d) To discuss the mode of origin of the deposits.

Some chemical analyses of the Kuttung lavas will be cited, and petrographic details sufficient to justify the determination of some of the rocks as *ignimbrites* will be given. However, full chemical study and critical textural and mineral- ogical investigations will be necessary before one can appreciate fully the remark- able vulcanicity of Carboniferous times in N.S.W.

FRAMEWORK SEQUENCE OF THE LOWER KUTTUNG.

(a) *The Lower Hunter Region.*

In 1919 (p. 288) W. R. Browne pointed out the general character of the Kuttung lava sequence, drawing attention to the main feature of a general decreasing basicity, with concentration of andesites at the base of the Volcanic Stage, of dacitic and toscanitic rocks in the central portion, and of rhyolitic types in the upper part. He gave a succinct account of the mineralogical and textural relationships of the lavas, as then known.

In 1925 the writer stated the following as the framework sequence for the Clarencetown-Paterson District (No. 1 being the oldest unit) :

7. Dacites.
6. Potash Rhyolites.
5. Toscanite-Dellenite Group (Mt. Gilmore Type).
4. Dacites.
3. Quartz Keratophyres (Williams River Type).
2. Pyroxene Andesites (Hudson's Peak Type).
1. Hornblende Andesites (Martin's Creek Type).

As pointed out by various workers, there are many places where the framework sequence is much extended or " filled-out ", as it were, by an abundance of lavas and tuffs which are peculiar to the respective localities of occurrence, and which sometimes present unusual features.

This is particularly the case with the Eelah-Gosforth District (Browne, 1926) and the Stanhope District (Scott, 1947). In the former there are acid rocks below the andesites of the Volcanic Stage, and there is a repetition of hornblende and pyroxene andesite units. In the Stanhope District a remarkable development of intermediate and acid rocks underlies those lavas which throughout the Lower Hunter, are regarded as marking the beginning of eruptions in the Volcanic Stage.

Correlations of the Sequences in the Lower Hunter Areas.

Not much has been published regarding the correlation of outstanding lavas and tuff horizons in the Lower Kuttung Series, although various workers

have had the subject much in mind, and considerable discussion has been engaged in, so that some ideas have become fixed regarding the equivalence of certain indicator horizons in separated localities.

Sussmilch (1923) set up certain correlations of sections in the Volcanic Stage but made some deductions which have proved erroneous. Browne (1926) explained certain broad correlations between the Gosforth District and the type areas further east. Miss Scott (1947) attempted to effect some detailed correlations between the Stanhope-Gosforth area and the type-area, and illustrated her views with columnar sections. In regard to these the author would venture the opinion that not all the suggested correlations are correct. First, though the basal andesites of the Volcanic Stage in the Seaham-Clarencetown area are correctly linked with similar flows at Gosforth and Stanhope, the higher andesites found in the latter places have no counterparts in the type-area. Secondly, in spite of his original statement (Osborne, 1922, 167) the author is not now satisfied that the Basal Stage as exposed in the type-area is present at Gosforth and Stanhope, since the sequence so designated there by Miss Scott has hitherto yielded no traces of the characteristic flora. It includes a number of lava-flows, and is perhaps better regarded as a downward extension of the Volcanic Stage.

The following correlations are given here as a result of mature consideration of the Kuttung succession across the whole of the Lower Hunter-Karuah region

(1) *The Martin's Creek Andesite Horizons (lithoidal and glassy)* may be traced from the Girvan District, on the east, through the Volcanic Stage belt which runs along the western side of the Stroud-Gloucester Trough. The andesite outcrops on the roadside about six miles east of Dungog and continues southwards to Clarencetown. (Beyond this point the regional distribution in the type area has already been published.) It can then be traced northward from Paterson towards Gresford, and suffers much faulting between this locality and Gosforth-Stanhope. The strict correlation in the latter area equates the horizons on the lower slopes of Hudson's Peak with those of Martin's Creek. These horizons of Hb. Andesite do not occur to the west or north of the Cranky Corner-Glendonbrook district. The intervention of the Webber's Creek fault and the Hunter Thrust have cut out possible extensions.

(2) *The Hudson's Peak type of pyroxene andesite and pitchstone* can be traced almost as satisfactorily as the amphibole types. The areas of greatest development are at Hudson's Peak, Stanhope and Balikera, near Seaham. West of the Stanhope area there are several flows of this type in the areas near the Hunter Thrust Line and elsewhere. In almost every case the associated strata indicate the validity of correlating them with the lower units found on Hudson's Peak.

(3) *The Williams River Quartz Keratophyre* is an intensely albitised dacite or toscanite, according to the area chosen. It does not occur in the Karuah Valley but can be traced from Limeburner's Creek through the complexly-faulted areas westward to Vacy and Gresford, eventually to appear at Eelah, Gosforth and Stanhope, being the first important flow to succeed the upper Hb. Andesites of those districts. Beyond this locality this horizon is absent from the sequence.

(4) *The Mt. Gilmore Toscanite-Dellenite Group,* over a wide area, has been proved a most reliable stratigraphical index.

This horizon varies through a limited range of composition, and also varies somewhat in texture, but is mostly medium to coarse-grained in its phenocrystic content.

A great development of this unit is seen around the nose of the Girvan anticline, east of Booral, and especially also along its western side. Thus the

rugged hills flanking the Lower Karuah River on the east side are made of thick flows of this rock.   The dominant ridges of toscanite on either side of the Stroud-Gloucester Trough are directly to be correlated with the Mt. Gilmore horizon.

Beyond the type area, the toscanite is found strongly developed at Eelah Gap and along the Rosebrook Ridge westward to Stanhope.   West of Glendon-brook it peters out and is unknown from the great areas of Volcanic Stage rocks in the middle Hunter Valley.

With few exceptions we cannot confidently correlate the many horizons of dacite, soda rhyolite, potash rhyolite and sodi-potassic types across areas of significant dimensions.   Some very local linkings can be made, of course. The main point to emphasise, however, is that acid and sub-acid rocks are characteristic, as a group, of the top of the Volcanic Stage.

(b) The Middle Hunter Region.

The Kuttung Belt which outcrops along the north-eastern side of the Middle Hunter Valley displays a sequence in the Volcanic Stage which is distinctly different from that of the areas dealt with above.

The important Kuttung areas in the Middle Hunter region are the Mirrannie-Dyrring, Glennie's Creek-Muswellbrook and the Mid-Rouchel-Bowman's Creek districts.

The framework sequence is incomplete because of the truncating effect of the Hunter Thrust all along the bounding zone between Glendonbrook and Muswellbrook.

The chief features of the sequence are :

(a) The presence of the pyroxene andesite in the lower stratigraphical zones.

(b) The abundance of *ignimbrites,* viz. on four main horizons, previously described as the Bridgman, Sedgefield, Westbrook and Glendonbrook Felsites (Osborne, 1926).

(c) The concentrated incidence of dacites a little above the topmost *ignimbrite.*

(d) The remarkably constant development of flows of typical Hb. Andesite at the top of the Volcanic Stage.

The skeleton sequence, therefore, is as follows, proceeding from older to newer : pyroxene andesites, ignimbrites, dacites and hornblende andesitic pitchstones. Various local modifications occur in this province, the chief examples being (a) the development of a group of spherulitic lavas in the Cross Creek area, north-west of Singleton, and (b) the appearance of an extra group of hornblende andesites in the Muscle Creek Section.

LOWER KUTTUNG TUFFS, FLOW-BRECCIAS AND RELATED TYPES.

Throughout the Lower Kuttung there is a great development of true pyroclastic rocks and of tuffaceous deposits which are due to admixture of ash and sedimentary units accumulated mainly sub-aqueously, but occasionally in a piedmont environment.   The more strictly igneous of the tuffaceous groups are medium to fine-grained, and show wide variation of composition, with a preponderance of biotite-dacite tuff in the lowermost zones and a predominance of soda-rhyolite tuff in the upper levels of the succession.

The totally pyroclastic rocks comprise (a) autobrecciated rhyolites, dacites and felsites, and (b) agglomerate and breccia formed by the accumulation of falling fragments from paroxysmal eruptions of fairly restricted extent.

Since recording in earlier papers the occurrence and petrography of many of these clastic rocks, the writer has been assembling data concerning their relationships with the facts of sequence and composition of the flows in the various neighbourhoods.

It can now be assumed that specialised centres of eruption have been responsible for great variety and overlapping of small flows in areas where flow-breccias and shatter-agglomerates are developed.

Following this line of enquiry it now becomes possible to postulate centres of eruption having considerable influence in overlapping, yet not controlling the distribution of the leading flows of the framework sequence.

Thus, partly based on the evidence of the tuff and breccia occurrences, we recognise the following centres in the Lower Kuttung :

(a) Muscle Creek, east of Muswellbrook.
(b) Cross Creek, north of Singleton.
(c) Bridgman District.
(d) Mirannie Area.
(e) Breckin Area.
(f) Gosforth District.
(g) Stanhope District.
(h) Pokolbin District.
(i) Martin's Creek District.
(j) Glenoak District.
(k) Mt. Gilmore, near Clarencetown.
(l) Booral and East Stroud.
(m) North Stroud-Weistmantels.

All through the present discussion it has been assumed that the framework sequence which holds so well over widespread localities, covering as much as 3,000 square miles, is the expression of a regional magmatic differentiation, and a regional control in serial eruptions, based upon widespread fissuring throughout large tracts whose geotectonic condition was related to a tensional environment, dependent upon gravity or isostatic controls.

VULCANICITY OF THE UPPER KUTTUNG SERIES.

The chief features of the volcanic succession in the Upper Kuttung Series in the region under notice are :

(i) The widely developed toscanite-dellenite lavas of the Paterson Type, which occupy a constant stratigraphical position.

(ii) The specialised occurrence of varied lava sequences in the upper part of the Glacial Stage.

It is clear that the Paterson lavas and associated pumiceous tuffs indicate the widespread revival of volcanic activity marked by fissure eruptions of a toscanite almost identical with an earlier fissure product (the Mt. Gilmore Toscanite). The Paterson Type has been studied from the whole of the Kuttung Belt lying between Raymond Terrace and the Mirannie-Bowman's Creek region. Beyond this the flows die out and are absent from the Upper Hunter Kuttung areas. The rocks grade from toscanite to dellenite, but as a group are markedly constant, petrologically.

High up in the Glacial Stage at Pokolbin, and also at Stanhope and Stroud, there is a noteworthy development of lavas embracing alkaline types such as trachyte and trachy-basalt, also flows of basalt. Small amounts of basalt have been recorded from elsewhere, but in the Stroud-Weistmantels sector there is a strong development of the basic rock.

It is clear that towards the end of Kuttung time there was developed, in response to local stress conditions, a series of strongly differentiated centres of

magmatic activity, by which the usual calcic series of andesite-dacite-rhyolite was modified by the incoming of alkaline types.   At the same time basalts with alkaline affinities began to appear.   Until considerable chemical and petrological information regarding these basalts is forthcoming it would be inadvisable to endeavour to relate them to the Kuttung sequences.

The presence of ignimbrites in the Glacial Stage at Stroud is a feature of Kuttung vulcanicity hereabouts.   Two horizons are well represented (see section below).   The outcrops of the upper ignimbrite to the west of the Pacific Highway about 1¼ miles south of Stroud Road recall vividly the field appearance of the well-known New Zealand type, Wilsonite, described by Marshall.

CHEMICAL ANALYSES

Below is given a list of analyses of representative lava-members of the Kuttung Succession.   It is to be regretted that no unit which can be confidently interpreted as an ignimbrite has been analysed.   No worth-while petrogenic discussion of the Kuttung lavas is yet possible, because so many of the rocks have been profoundly altered by deuteric processes, especially that of *albitisation*. Until a much greater amount of chemical data is available, one deprecates any attempt to discuss, more or less comprehensively, the chemical problems of the Kuttung vulcanicity.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO_2 ..	64·20	64·88	61·10	67·06	73·04	73·90	72·98	77·82	75·06
Al_2O_3	16·88	16·18	16·20	15·95	13·86	11·95	12·58	11·46	14·21
Fe_2O_3..	1·90	1·52	2·00	1·78	1·60	1·70	0·28	0·30	1·31
FeO ..	2·52	2·43	3·78	2·37	0·45	0·99	1·66	0·09	0·27
MgO	0·66	1·21	3·55	1·87	0·48	0·55	0·49	0·23	0·09
CaO ..	3·14	3·00	4·90	1·98	1·44	1·50	2·81	0·22	0·42
Na_2O	4·41	5·41	3·42	4·62	3·40	3·10	4·80	0·86	6·88
K_2O	3·52	2·79	2·83	2·01	4·39	4·74	2·99	7·19	0·58
H_2O+	1·79	1·63	1·03	0·65	0·79	1·37	0·79	1·40	0·62
H_2O-	0·31	0·50	0·53	0·44	0·25	0·21	0·43	0·36	0·56
CO_2 ..	0·03	tr.	abs.	abs.	abs.	abs.	abs.	0·03	—
TiO_2 ..	0·65	0·89	0·55	0·40	0·22	0·20	0·40	0·02	abs.
P_2O_5 ..	0·13	tr.	0·21	0·28	0·04	0·05	0·08	0·04	0·03
MnO ..	—	0·05	tr.	0·39	0·07	0·06	0·03	tr.	0·04
BaO .. etc.	—	—	tr.	—	0·04	0·06	—	0·02	—
	100·14	100·49	100·10	99·80	100·07	100·38	100·32	100·04	100·07

    I. Hb. Andesite, Martin's Creek.   Anal. G. D. Osborne.
   II. Hb. Andesite, Martin's Creek.   Anal. W. G. Stone.
  III. Pyroxene Andesite (Hudson's Peak Type), Pokolbin.   Anal. W. A. Greig.
  IV. Qtz. Keratophyre (Williams River Type), Clarencetown.   Anal. G. D. Osborne.
   V. Toscanite, Mt. Gilmore.   Anal. W. A. Greig.
  VI. Toscanite (Mt. Gilmore Type), Port Stephens.   Anal. W. G. Stone.
 VII. Toscanite, Paterson.   Anal. G. D. Osborne.
VIII. Rhyolite, Mt. Bright, Pokolbin.   Anal. J. C. H. Mingaye.
  IX. Soda Rhyolite, Paddy's Hill, north of Raymond Terrace.   Anal. W. A. Greig.

THE IGNIMBRITES.

Previous Recognition of Ignimbrites in the Kuttung Succession.

In 1923 the writer visited New Zealand and studied the occurrence and petrography of the ignimbrites of the North Island, after the advantage of full discussion of these rocks with Dr. P. Marshall, who first interpreted the rhyolitic

rocks of the Great Volcanic Plateau as compacted material ejected as *nuées ardentes* (Marshall, 1932). Subsequently, in 1934, in an address to the Geological Section of the Royal Society of N.S.W. upon the N.Z. ignimbrites (see THIS JOURNAL, Vol. 68, p. xlviii), specimens of certain Kuttung rocks were exhibited and the opinion expressed that these were ignimbrites.

Quite recently Beryl Scott (1947) has recorded the presence of ignimbrites in the Volcanic Stage in the Stanhope District, and has given somewhat meagre metrographic accounts of these.

Since suggesting an ignimbritic origin for many of the volcanic units hitherto described from the Kuttung as rhyolites, and rhyolitic tuffs, the writer has been assembling evidence of the widespread occurrence of these fascinating rocks in the Hunter and Karuah River Districts.

(It is pertinent to mention here that in 1934 H. C. Richards and W. H. Bryan discussed the mode of origin of part of the Brisbane Tuff and concluded that it paralleled very closely the ignimbrites of New Zealand.)

Field Occurrence.

The ignimbrites of the N.S.W. Carboniferous are distinctive in their field relations, occurring in relatively thin units which are remarkably persistent over large areas. The thickness varies up to a maximum of 120 feet, but generally is small and of the order of 12–20 feet. The rocks are light coloured with marked " fluidal " texture, and show in many areas a rude prismatic jointing more or less perpendicular to the " flow structure ". This jointing does not pass into the associated rocks, nor is it related genetically to any tectonic features of the surrounding country. It is essentially syngenetic, and this recalls the prevalence of syngenetic jointing in the New Zealand ignimbrites. Marshall interprets this as evidence against a rock with flow structure consolidating from a molten condition. (It is interesting to note that in several early papers published by the writer before the concept of ignimbrites was forthcoming, reference to this jointing was made, although its significance was not known.)

It always has been difficult to explain the " flow " structures and the extremely extended outcrops of the ignimbrites, if they were to be regarded as acid flows. With high viscosity characteristic of the rock-types under consideration, considerable flowing of the magma would have been unlikely, and the regularity of the flow-layers would almost certainly have been obliterated or modified by flow-breccia structures.

In two or three places in the Middle Hunter area it is possible to see evidence that the ignimbrite was developed on a very uneven floor, and reconstruction of the physiography of the localities in question indicates that the igneous rock (if a flow) travelled " uphill " considerably. With more and more field work in recent years, it has become necessary to invoke some special mode of development different from accepted ideas of the ordinary flow of lava, to explain the units now being discussed. Accordingly I have concluded that the rocks in question have had essentially the same mode of origin as the ignimbrites described by Marshall. Some fuller explanation of this view is given below.

Petrography.

The ignimbrites vary in grainsize, and may be very heterogeneous on a small scale, while at other times exhibiting an even-textured " ground " through which are strung axiolites, beaded concentrations of spherulites, and comb-like structures in fibrous felspathic and siliceous material. Many shards and tubes of pumice and myriad cuspate fragments and shreds of glassy material are packed into a solid mass with pseudo-fluidal texture, giving distinctive fracture and variable lustre from surface to surface.
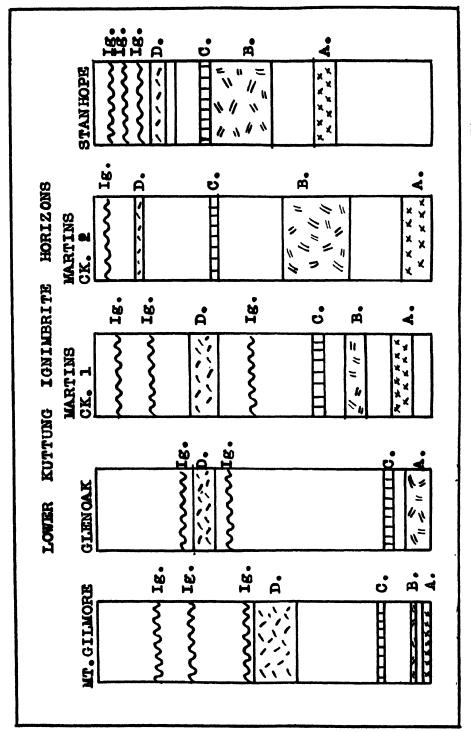
Fig. 1.—A. signifies Martin's Creek horizon. B. Hudson's Peak horizon. C. Williams River horizon. D. Mt. Gilmore horizon. Ig. Ignimbrite. Thickness of sections given in text. (*Note.*—In the Glenoak Section the lowest unit should be marked B, not A.)

There is a suggestion of dense silicification or of devitrification in many rocks. While patches are glassy, the bulk of the rocks are now lithoidal or felsitic.

The rocks show no scoriaceous or ropy texture at the upper surface, although the apparent flow structure is so marked in the body of the rock. Uniformity of colour (mostly pink or cream) is a feature over wide areas and there is an absence of abrupt passage from fluidal rock into brecciated material, such as is seen with many of the normal Kuttung flows. No autoclastic structure or twisted flow-fabric occurs in the ignimbrites, such as is seen in modern lavas whose origin is not in doubt.

Microscopically, the ignimbrites are very difficult of satisfactory study, and it is not proposed to discuss the petrography in full, as this will be taken along with a chemical study of these rocks in the future. It is sufficient to note that the " phenocrystic " minerals commonly developed are quartz, oligoclase or albite, biotite, and a variable amount of orthoclase. Rarely altered hornblende is seen, and occasionally one or two pieces of what appear to be hypersthene. These units (of approximately uniform grainsize up to a maximum of 2 mm.) are set in a devitrified pumiceous groundmass of fine silica and felspathic material, through which are threaded abundant axiolitic and genetically kindred structures.

Many of the tubular or shred-like fragments bend around the " phenocrysts " of albite and quartz and indicate clearly a plastic condition prior to crystallisation.

Stratigraphical Horizons.

Text-figure 1 indicates the stratigraphical relationships of the ignimbrite deposits, the chronological positions of the postulated eruptions being summarised thus :

(a) There is a pronounced concentration towards the upper part of the Volcanic Stage, the Stanhope Section being the only one in which an ignimbrite has been recorded from low down in the sequence.

(b) Within the Volcanic Stage most of the ignimbrites are above the horizon of the Mt. Gilmore toscanite although in two sections an ignimbrite zone marks the infra-toscanite series.

(c) In the Glacial Stage there are two ignimbrite horizons, these being respectively below and above the horizon of the Paterson toscanite.

It would thus appear that the special eruptive conditions for the production of ignimbrites obtained at several distinct times in the areas now being considered. These violent conditions occurred in the Upper Volcanic Stage and the Mid-to-Upper Glacial Stage.

DETAILED STRATIGRAPHICAL SECTIONS SHOWING IGNIMBRITE HORIZONS.

It is proposed in this section to restate certain sections of the Volcanic Stage, already published, and to record a new section from the Glacial Stage, for the purpose of placing on record the stratigraphical positions, and the stratigraphical concentration of ignimbrites in the Kuttung succession. (All sections descend stratigraphically.)

(a) *The Mt. Gilmore Section* (Osborne, 1922, p. 172).

	Feet
Tuffs	45
Volcanic conglomerate	50
Tuffs with pebbly bands	130
Potash rhyolite	50
Ignimbrite	50
Conglomerate	80
Potash rhyolite	40
Conglomerates	90

Keratophyre		90
Conglomerate		50
Ignimbrite		100
Red potash rhyolite		60
Conglomerate		150
Ignimbrite		70
Tuffaceous conglomerate		45
Ignimbrite		60
Tuffs with felsite		80
Dellenite-Toscanite (Mt. Gilmore Type)		400
Conglomerate		320
Rhyo-dacite		150
Bi. Qtz. keratophyre (Williams River type)		105
Conglomerate		30
Bi. Qtz. keratophyre (Williams River type)		150
Conglomerate		75
Sodi-potassic rhyolite		45
Conglomerate		80
Pyroxene andesite (Hudson's Peak type)		50
Pebbly tuff		150
Hornblende andesite (Martin's Creek type)		80

Total 2,875

(b) *The Glenoak Section* (Osborne, 1922, p. 175).

		Feet
Dacite		120
Sodi-potassic rhyolite		45
Ignimbrite		130
Rhyolite		250
Dellenite (Mt. Gilmore type)		80
Conglomerate		45
Ignimbrite		40
Fine-grained quartz keratophyre		90
Conglomerate		450
Felsite		60
Conglomerate		180
Fine tuff		60
Coarse tuff		100
Volcanic conglomerate, etc...		60
Bi. Qtz. keratophyre (Williams River type)		180
Pebbly tuff		100
Pyroxene andesite glass (Hudson's Peak type)		200

Total 2,190

(c) *Martin's Creek, Section No.* 1 (Osborne, 1922, p. 177).

		Feet
Tuffs		200
Ignimbrite		30
Dacite		100
Flow-breccias		80
Ignimbrite		25
Pebbly tuff		185
Toscanite (Mt. Gilmore type)		210
Tuffaceous conglomerate		200
Ignimbrite		80
Tuff		70
Conglomerate		65
Bi-Qtz. keratophyre (Williams River type)		85
Conglomerate		100
Pyroxene andesite (Hudson's Peak type)		80
Pebbly tuff		100
Hornblende andesite (Martin's Creek type)		200

Total 1,810

(d) *Martin's Creek, Section No. 2* (Osborne, 1922, p. 178).

	Feet
Ignimbrite	50
Cherty tuff	25
Fine-grained tuffs	15
Volcanic conglomerate	10
Conglomerate	15
Toscanite (Mt. Gilmore type)	50
Soda-felsite	100
Red potash-rhyolite	25
Coarse conglomerate	300
Bi-Qtz. keratophyre (Williams River type)	50
Total	640

(e) *The Stanhope Section* (Scott, 1947).

	Feet
Dacite tuffs with several *Ignimbrite* horizons (relatively thin)	800
Toscanite (Mt. Gilmore type)	260
Conglomerate	180
Toscanite (on horizon of Williams River keratophyre)	400
Hornblende andesite	900
Pyroxene andesite (Hudson's Peak type)	1,200
Conglomerate	350
Hornblende andesite (Martin's Creek type)	130
Conglomerate	160
Ignimbrite	30
Conglomerate	250
Felsite	130
Fluvio-glacial conglomerate	450
Pyroxene andesite	50
Conglomerate	50
Rhyolite	920
Pyroxene andesite	660
Conglomerate	100
Rhyolite	?
Total, at least	7,020

(f) *The Bridgman Section* (Osborne, 1926, p. 391).

	Feet
Hornblende andesite	200
Conglomerate and tuff	150
Hornblende andesite	50
Conglomerate	170
Hæmatitic flow-breccia	20
Ignimbrite	30
Felsite	15
Ignimbrite	20
Conglomerate with hæmatitic lava band	250
Ignimbrite	30
Conglomerate	220
Ignimbrite	30
Conglomerate and tuffs	150
Ignimbrite	40
Conglomerate and tuff	60
Total	1,435

(g) *The Muscle Creek Section* (Osborne, 1928, p. 568).

	Feet
Tuffaceous conglomerate	300
Felsite	80
Tuffaceous conglomerate	200
Dacite	100
Coarse conglomerate	400
Biotite felsite	50

Conglomerate	..	..	..	..	..	..	..	..	300
Hb. andesite glass	..	..	..	..	..	..	..	..	80
Conglomerate	..	..	..	..	..	..	..	..	200
Fine tuff	..	..	..	..	..	..	..	..	300
Coarse tuff	..	..	..	..	..	..	..	..	100
Acid tuff	..	..	..	..	..	..	..	..	170
Conglomerate	..	..	..	..	..	..	..	..	100
Andesitic conglomerate	..	..	..	..	..	..	..	..	90
Soda felsite	..	..	..	..	..	..	..	..	60
Conglomerate	..	..	..	..	..	..	..	..	200
Tuff	..	..	..	..	..	..	..	..	80
Dacites (devitrified)	..	..	..	..	..	..	..	..	245
Tuff	..	..	..	..	..	..	..	..	100
Ignimbrite	..	..	..	..	..	..	..	..	120
Coarse tuff	..	..	..	..	..	..	..	..	300
Ignimbrite	..	..	..	..	..	..	..	..	150
Tuff and conglomerate	..	..	..	..	..	..	..	..	200
Dacite	..	..	..	..	..	..	..	..	170
Tuff and conglomerate	..	..	..	..	..	..	..	..	95
Ignimbrite	..	..	..	..	..	..	..	..	85
Tuff	..	..	..	..	..	..	..	..	200
Soda felsite	..	..	..	..	..	..	..	..	90
Tuff and conglomerate	..	..	..	..	..	..	..	..	230
	Total	..	..	..	..	..	..	..	4,795

(h) *The Stroud Section (Generalized).*

									Feet
Basalt	..	..	..	..	..	..	..	..	200
Andesitic tuff	..	..	..	..	..	..	..	..	150
Ignimbrite	..	..	..	..	..	..	..	..	25
Conglomerate	..	..	..	..	..	..	..	..	20
Hb. andesite	..	..	..	..	..	..	..	..	20
Rhyolite	..	..	..	..	..	..	..	..	25
Dacite	..	..	..	..	..	..	..	..	50
Coarse conglomerate	..	..	..	..	..	..	..	..	30
Tuffs with pebbles	..	..	..	..	..	..	..	..	560
Basalt	..	..	..	..	..	..	..	..	150
Rhacopteris tuff	..	..	..	..	..	..	..	..	20
Conglomerate	..	..	..	..	..	..	..	..	100
Ignimbrite	..	..	..	..	..	..	..	..	15
Sandy tuffs	..	..	..	..	..	..	..	..	120
	Total	..	..	..	..	..	..	..	1,485

MODE OF ORIGIN OF THE IGNIMBRITES.

It is the opinion of the writer that the ignimbrites here discussed have been formed after the manner described by Marshall for the N.Z. occurrences. That is to say they are due to the welding together of tuffaceous material given out in the incandescent state from fissures, and carried with swift velocity to places of accumulation. Thus they are the products of a series of *nuées ardentes*.

It is considered that the eruptions were of the *Katmaian Type*, in the nomenclature of Lacroix. This type, as opposed to the *Pelean* eruption (which takes place in a restricted crater) involves the supply of material from fissures. It is essential, in considering the origin of these fascinating rocks, that we should draw from the experience that scientists have had in observing modern eruptions of the " glowing cloud " or *nuée ardente* type. Fortunately the literature upon this subject is already considerable, and reputable geologists and petrologists have described phenomena observed by them, or have carefully investigated the recent products of outbursts of this kind. (See Flett, 1908 ; Jagger, 1903 ; Perrett, 1935 ; Lacroix, 1904 ; Macgregor, 1936, 1938 ; .and Marshall, 1932, 1935). Thus we may postulate that shreds and chips of glassy material have

been produced by a frothing over and instantaneous shattering of pumiceous lava very rich in gas. Fairly large volumes of finely divided material have been involved in the accumulation of some of the thicker ignimbrites.

It is probable that in the areas of the Lower and Middle Hunter in Kuttung times there were alternations of eruptive controls, so that three types of vulcanicity affected the region from time to time. These were responsible at different epochs for

(a) welling out of lava flows from fissures ;

(b) explosive discharge of ash, pumice, tuffs, boulders, lapilli, etc., all at a temperature such that on falling to the ground no further vulcanological processes would be likely to continue ;

(c) intensively gaseous and explosive eruptions of the *nuée ardente* type.

Apparently some of the products due to the second type of control would be pure tuffs or breccias while others would be contaminated by sediment. Very local eruptions would produce agglomerate and breccia-filled necks. In cases of eruptions of type (a), two cases would arise. Either homogeneous lava not greatly charged with volatiles would spread uniform flows over wide areas, or inhomogeneous lava would give rise to streaky and layered extrusions. Both products are encountered in the Kuttung fields, but the former is, of course, the prevalent type. An example of the latter is that of the heterogeneous felsite at the foot of the Hudson's Peak Section, near Gosforth.

Prevalence of Gas in Ignimbrite Eruptions.

Vulcanologists who have studied the origin and mode of accumulation of *nuées ardentes* emphasise that an important determining factor in the sudden development of an incandescent cloud from partly consolidated rock material and volcanic gases is the course of the gas-history in the time just prior to the climax of eruption. If gas is prevented from escaping from the vent, the lava is unrelieved by effervescence and the condition is reached when expansion produces a frothing pumice due to violent action breaking through any residual crust. Thus is caused the ejection of incandescent material. Reactions between liberated gases help to keep glowing the various fragments (large and small). Solidification of glassy blebs will set free gas, thus producing porous texture in some of the solid ingredients of a *nuée ardente*.

It is clear that the various grades of material which have frothed over will settle down in some sort of density-controlled stratification, even though the accumulation has been rapid and of avalanche character.

Rocks similar to the ignimbrites of New Zealand have been formed by recent or modern eruptions in the West Indies, Katmai Province of Alaska, Yellowstone National Park, Crater Lake (Oregon) and elsewhere (see Bibliography).

SUMMARY.

An account is given of the salient features of the Kuttung Vulcanicity in the Hunter-Karuah District, particular attention being given to the occurrence of welded pumiceous tuffs, known in New Zealand as *ignimbrites*. The stratigraphical incidence of the *ignimbrite* horizons is made clear by the statement of many detailed sections from the area. These fascinating units in the volcanic succession are shown by their features of (a) texture, (b) field occurrence, and (c) vulcanological environment, to correspond almost exactly to products of the Katmaian type of the *nuée ardente* type of eruption.

BIBLIOGRAPHY.

Browne, W. R., and Walkom, A. B., 1911. THIS JOURNAL, **45**, 379.

Browne, W. R., 1919. THIS JOURNAL, **53**, 287.

—————————— 1926. THIS JOURNAL, **60**, 213.

Carey, S. W., and Browne, W. R., 1937. THIS JOURNAL, **71**, 591.

Fenner, C. N., 1920. *Jour. Geol.*, 569.

Flett, J. S., 1908. *Philos. Trans., A*, **208**, 305.

Jaggar, T., 1903. *Amer. Naturalist*, **38**, 51.

Lacroix, A., 1904. La Montagne Peleaetses Eruptions. (Paris.)

Macgregor, A. G., 1936. *Proc. Roy. Soc., B*, **121**, 232.

—————————— 1938. *Philos. Trans.*, Ser. B, **229**, 1.

Osborne, G. D., 1922. *Proc. Linn. Soc. N.S.W.*, **47**, 161.

—————————— 1925. *Proc. Linn. Soc. N.S.W.*, **50**, 112.

—————————— 1926. *Proc. Linn. Soc. N.S.W.*, **51**, 387.

—————————— 1928. *Proc. Linn. Soc. N.S.W.*, **53**, 565.

Perrett, F. A., 1935. *Carn. Institn.*, Pub. No. 458.

Richards, H. C., and Bryan, W. H., 1934. *Proc. Roy. Soc. Qsld.*, **70**, 50.

Scott, Beryl, 1947. THIS JOURNAL, **81**, 221.

Sussmilch, C. A., 1923. THIS JOURNAL, **57**, 12.

Williams, Howel, 1941. *Univ. Cal. Publ.*, 7 ; *Bull. Dep. Geol. Sci.*, **25** (6), 272.

Marshall, P., 1932. *N.Z. Journ. Sci. Tech.*, **13**, 198.

—————————— 1935. *Trans. Roy. Soc. N.Z.*, **64**, 1.

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1942	P 1	Jaeger, John Conrad, M.A., D.sc., University of Tasmania, Hobart, Tasmania.
1909	P 15	Johnston, Thomas Harvey, M.A., D.sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1949		Joklik, Gunther F., B.sc., c.o. Bureau of Mineral Resources, Canberra, A.C.T.
1935	P 6	Joplin, Germaine Anne, B.sc., Ph.D., 18 Wentworth-street, Eastwood.
1948	P 1	Jopling, Alan Victor, B.sc., B.E., 28 Cliff-street, Manly.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1935		Kelly, Caroline Tennant (Mrs.), Dip.Anth., " Eight Bells," Cast Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
· 1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney ; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.s.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove.
1948		Kimble, Frank Oswald, Engineer, 16 Evelyn-avenue, Concord.
1943		Kimble, Jean Annie, B.sc., Research Chemist, 383 Marrickville-road, Marrickville.
1920		Kirchner, William John, B.sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo ; p.r. 18 Lyne-road, Cheltenham.
1948		Knight, Oscar Le Maistre, B.E. *Syd.*, A.M.I.C.E., A.M.I.E.Aust., Engineer, 10 Mildura-street, Killara.
1948		Koch, Leo E., Ph.D., D.sc. (*Cologne*), Department of Geology, The University of Sydney ; p.r. 39 Bond-street, Mosman.
1939	P 1	Lambeth, Arthur James, B.sc., " Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1949		Lancaster, Kelvin John, B.sc., 43 Balfour-road, Rose Bay.
1936		Leach, Stephen Laurence, B.A., B.sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., Box 21, P.O., Concord.
1946		Lederer, Michael, 67 Edgecliff-road, Bondi Junction.
1947		Le Fevre, Raymond James Wood, D.sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney.
1936	P 2	Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 56	‡Lions, Francis, B.sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.)
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1947		Lloyd, James Charles, B.sc. *Syd.*, N.S.W. Geological Survey, 41 Goulburn-street, Liverpool.
1940	P 1	Lockwood, William Hutton, B.sc., c.o. Institute of Medical Research, The Royal North Shore Hospital, St. Leonards.
1906		‡Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1949		Loughnan, Frederick Charles, " Bodleian ", 26 Kenneth-street, Longueville.
1947		Lowenbein, Gladys Olive (Mrs.), B.sc. *Melb.*, F.R.I.C. Gt. B., A.A.C.I., Director of Research, Australian Leather Research Association ; p.r. 5 Berrima Flats, 12 Mulwarrie-avenue, Randwick.
1943		‡Luber, Daphne (Mrs.), B.sc., 98 Lang-road, Centennial Park.
1945		Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1948	P 2	Lyons, Lawrence Ernest, B.A., M.sc., Lecturer in Chemistry, The University of Sydney ; p.r. 13 Albert-road, Strathfield.
1942		Lyons, Raymond Norman Matthew, M.sc., Biochemical Research Worker,

Elected.

Elected	P No.	Entry
1939	P 4	Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1949		McCarthy, Frederick David, Curator of Anthropology, Australian Museum, Sydney; p.r. 10 Tycannah-road, Northbridge.
1943		McCoy, William Kevin, Analytical Chemist, c/o Mr. A. J. McCoy, 39 Malvern-avenue, Merrylands.
1949		McElroy, Clifford Turner, 147 Arden-street, Coogee.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1948		McInnes, Gordon Elliott, Department of Geology, The University of Sydney; p.r. 46 Laycock-street, Bexley.
1906	P 2	‡McIntosh, Arthur Marshall, " Moy Lodge," Hill-street, Roseville.
1944	P 7	McKenzie, Hugh Albert, B.Sc., 52 Bolton-street, Guildford.
1943	P 1	McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo; p.r. Flat 2, 42A, Waimea-street, Burwood.
1947		McMahon, Patrick Reginald, M.Agr.Sc. *N.Z.*, Ph.D. *Leeds*, A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney.
1927		McMaster, Sir Frederick Duncan, Kt., " Dalkeith," Cassilis, N.S.W.
1943		McNamara, Barbara Joyce (Mrs.), M.B., B.S., Yeoval, 7.W.
1946		McPherson, John Charters, 14 Narnar-road, Greenwich.
1946	P 1	McRoberts, Helen May, B.Sc., New England University College, Armidale.
1947		Magee, Charles Joseph, D.Sc.Agr. *Syd.*, M.Sc. *Wis.*, Chief Biologist, Department of Agriculture; p.r. 4 Alexander-parade, Roseville.
1947		Maley, Leo Edmund, M.Sc., B.Sc. (Hons.), A.A.C.I., A.M.A.I.M.M., 116 Maitland road, Mayfield.
1940		Malone, Edward E., 33 Windsor-road, St. Mary's.
1947	P 12	Mapstone, George E., M.Sc., A.A.C.I., M.In·t.Pet., Chief Chemist of National Oil Pty. Ltd., Glen Davis; p.r. 2 Anderson Square, Glen Davis, N.S.W.
1949		Marshall, Charles Edward, Ph.D., D.Sc., Professor of Geology, The University of Sydney, Sydney.
1944		Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1946		May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill.
1935	P 1	Maze, William Harold, M.Sc., Registrar, The University of Sydney, Sydney.
1949		Meares, Harry John Devenish, Technical Librarian, Colonial Sugar Refining Co. Ltd., Box 483, G.P.O., Sydney.
1912		‡Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Fairlight.
1929	P 25	Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.)
1928		Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, Jordan House, Jordan Terrace, Bowen Hills, Brisbane.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1922	P 28	Morrison, Frank Richard, A.A.C.I., F.C.S., Deputy Director, Museum of Technology and Applied Science, Harris-street, Ultimo.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn Street, Parramatta.
1934		Mort, Francis George Arnot, A.A.C.I., Chemist, 110 Green's-road, Fivedock.
1948		Mosher, Kenneth George, B.Sc., Geologist,·c.o. Joint Coal Board, 66 King-street, Sydney.
1944		Moye, Daniel George, Geologist, 6 First-avenue, Snowy Mountains Hydro-Electric Authority, Cooma, N.S.W.
1946		Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney.
1948		Mulley, Joan W., Technical Officer, C.S.I.R.; p.r. 4 Billyard-avenue, Elizabeth Bay.
1915		‡Murphy, Robert Kenneth, Dr.Ing., Chem., A.S.T.C., M.I.Chem.E., F.A.C.I., Principal, Sydney Technical College, Sydney.
1923	P 2	Murray, Colonel Jack Keith, B.A., B.Sc.Agr., Administrator, Territory of Papua-New Guinea, Government House, Port Moresby.
1948		Naylor, Betty Yvonne, B.Sc., 6 Niblick-avenue, Roseville.
1930	P 7	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld.
1943		Neuhaus, John William George, 190 Old Prospect-road, Wentworthville.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Professor of Botany, The University of Ceylon, Colombo, Ceylon.

Elected.		
1943		Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co. ; p.r. 200 Paine-street, Maroubra.
1935		Nicol, Phyllis Mary, M.SC., Sub-Principal, The Women's College, Newtown.
1945	P 1	Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T.
1938	P 1	Noble, Norman Scott, D.SC.AGR., M.SC., D.I.C., c/o C.S.I.R., 314 Albert-street, East Melbourne, Vic.
1920	P 4	‡Noble, Robert Jackson, M.SC., B.SC.AGR., PH.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney ; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
1947		Nordon, Peter, A.S.T.C., A.A.C.I., Chemical Engineer, 39 Tahlee-street, Burwood.
1948		Northcott, Jean, B.SC. (Hons.), Chemistry Department, The University of Sydney ; p.r. 38 Canberra-street, Lane Cove.
1940	P 25	Nyholm, Ronald Sydney, M.SC., Chemistry Department, University College, Gower-street, London, W.C.1, England.
1935	P 4	O'Connell, Rev. Daniel J. K., S.J., M.SC., D.PH., F.R.A.S., Riverview College Observatory, Sydney.
1947		Old, Adrian Noel, B.SC.AGR., Chemist, Department of Agriculture ; p.r. 4 Springfield-avenue, Pott's Point.
1921	P 11	Osborne, George Davenport, D.SC. *Syd.*, PH.D. *Camb.*, Lecturer and Demonstrator in Geology in the University of Sydney. (President, 1944.)
1920	P 75	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Director, Museum of Technology and Applied Science, Harris-street, Ultimo. (President, 1931.)
1949		Penrose, Ruth Elizabeth, B.SC., 92 Baringa-road, Northbridge.
1948		Perry, Hubert Roy, B.SC., 74 Woodbine-street, Bowral.
1938		Phillips, Marie Elizabeth, B.SC., Botany Department, University, Manchester, 13, England.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliff.
1946		Pinwell, Norman, B.A. (*Q'land*), The Scots College, Bellevue Hill.
1943	P 1	Plowman, Ronald Arthur, B.SC. *Lond.*, A.S.T.C., A.A.C.I., Analytical Chemist, 21 Harris-street, Normanhurst.
1919		Poate, Hugh Raymond Guy, M.B., CH.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney ; p.r. 38 Victoria-road, Bellevue Hill.
1949		Poggendorff, Walter Hans George, B.SC.AGR., Chief of the Division of Plant Industry, N.S.W. Department of Agriculture, Box 36A, G.P.O., Sydney.
1896		‡Pope, Roland James, B.A. *Syd.*, M.D., CH.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
1946		Potter, Bryce Harrison, B.SC. (Hons.) *Syd.*, 68 Wharf-road, Gladesville.
1921	P 2	Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney ; p.r. " Wansfell," Kirkoswald-avenue, Mosman.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1945		Prescott, Alwyn Walker, B.ENG., Lecturer in Mechanical and Electrical Engineering in the University of Sydney ; p.r. Harris-road, Normanhurst.
1927		Price, William Lindsay, B.E., B.SC., Teacher of Physics, Sydney Technical College ; p.r. 8 Wattle-street, Killara.
1918	P 1	Priestley, Henry, M.D., CH.M., B.SC., 54 Fuller's-road, Chatswood. (President, 1942-43.)
1945		Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood.
1893		‡Purser, Cecil, B.A., M.B., CH.M. *Syd.*, " Ascot," Grosvenor-road, Wahroonga.
1935	P 3	‡Quodling, Florrie Mabel, B.SC., Lecturer in Geology, University of Sydney
1922	P 6	Raggatt, Harold George, D.SC., Director, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, C.1, Victoria.
1940	P 2	Ralph, Colin Sydney, B.SC., 24 Canberra-street, Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.SC., B.E., 57 William-street, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1947		Ray, Nancy Evelyn (Mrs.), Plastics Manufacturer, 14 Hedger-avenue, Ashfield.

Elected.		
1949		Stanton, Richard Limon, B.SC., Teaching Fellow in Geology, The University of Sydney, Sydney ; p.r. 42 Hopetoun-avenue, Mosman.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		‡Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney ; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1948	P 1	Stevens, Neville Cecil. B.SC., Geology Department, The University of Sydney ; p.r. 12 Salisbury-street, Hurstville.
1900	P 1	‡Stewart, J. Douglas, B.V.SC., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney ; p.r. " Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.SC., Ph.D., Professor of Biochemistry, The University of Sydney, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney ; p.r. 26 Rosslyn-street, Bellevue Hill.
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes ; Box 23, P.O., Burwood ; p.r. " Stonycroft," 10 Redmyre-road, Strathfield.
1919		‡Sutherland, George Fife, A.R.C.SC. Lond., 47 Clanwilliam-street, Chatswood.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. Melb., B.SC. Oxon., Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney ; p.r. " Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.SC. Adel., c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.
1948		Swinbourne, Ellice Simmons, Organic Chemist, A.S.T.C., A.A.C.I., 1 Raglan-street, Manly.
1915	P 3	‡Taylor, Brigadier Harold B., M.C., D.SC., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney ; p.r. 12 Wood-street, Manly.
1944		Thomas, Andrew David, Squadron Leader, R.A.A.F., M.SC., A.Inst.P. 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic.
1946		Thomas, Ifor Morris, M.SC., Department of Zoology, University of Adelaide, Adelaide, S.A.
1946	P 1	Thompson, Nora (Mrs.), B.SC. Syd., c/o Australasian Petroleum Coy., Port Moresby, Papua.
1919		Thorne, Harold Henry, M.A. Cantab., B.SC. Syd., F.R.A.S., Lecturer in Mathematics in the University of Sydney ; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.SC., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
1923		Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.SC., No. 5, " Werrington," Manion-avenue, Rose Bay.
1949		Trebeck, Prosper Charles Brian, A.C.I.S., F.Com.A., Eng., A.F.I.A., A.A.A., J.P., 3 Honda-road, Neutral Bay.
1943		Turner, Ivan Stewart, M.A., M.SC., Ph.D., Lecturer in Mathematics, University of Sydney ; p.r. 120 Awaba-street, Mosman.
1949		Vallance, Thomas George, 57 Auburn-street, Sutherland.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.SC., Botanic Gardens, Sydney ; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, D.SC., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 10	‡Vonwiller, Oscar U., B.SC., F.Inst.P., Emeritus Professor of Physics in the University of Sydney ; p.r. " Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.)
1948		Walker, Donald Francis, Surveyor, 13 Beauchamp-avenue, Chatswood.
1943		Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping.
1919	P 2	Walkom, Arthur Bache, D.SC., Director, Australian Museum, Sydney ; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1913	P 5	‡Wardlaw, Hy. Sloane Halcro, D.SC. Syd., F.A.C.I., c/o Kanematsu Institute, Sydney Hospital, Macquarie Street, Sydney. (President, 1939.)
1944		Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T.
1921		‡Waterhouse, Gustavus Athol, D.SC., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett Illoura-avenue, Wahroonga.
1919	P 1	Waterhouse, Lionel Lawry, B.E. Syd., Lecturer and Demonstrator in Geology in the University of Sydney.

HONORARY MEMBERS.
Limited to Twenty.

OBITUARY, 1949–50.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke " as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories ; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and " The Origin of Dolomite " (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.

1907. "Geography of Australia in the Permo-Carboniferous Period " (two lectures). By Professor T. W. E. David, B.A., F.R.S.

" The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.

" Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.

" The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.

1918. " Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.

1919. " Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.

1936. " The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)

1937. " Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)

1938. " The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)

1939. " Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)

1940. " The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)

1941. " The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)

1942. " The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.

1943. " Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.

1944. " An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.

1945. " Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.

1946. " The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.

1947. " The Teachers of Geology in Australian Universities." By Professor H. S. Summers D.Sc.

1948. " The Sedimentary Succession of the Bibliando Dome : Record of a Prolonger Proterozoic Ice Age." By Sir Douglas Mawson, O.B.E., F.R.S., D.Sc., B.E.

1949. " Metallogenetic Epochs and Ore Regions in Australia." By W. R. Browne, D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.

1879 *George Bentham, C.M.G., F.R.S.

1880 *Professor Thos. Huxley, F.R.S.

1881 *Professor F. M'Coy, F.R.S., F.G.S.

1882 *Professor James Dwight Dana, LL.D.

1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.

1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

Awarded.

1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886 *Professor L. G. De Koninck, M.D.
1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., SC.D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., SC.D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.SC., F.G.S.
1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
1909 *Dr. Walter E. Roth, B.A.
1912 *W. H. Twelvetrees, F.G.S.
1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, M.A., D.SC., F.R.S.
1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., SC.D., D.SC., F.R.S., F.G.S.
1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.SC.
1922 *Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.SC., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., " Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 *Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
1929 Professor Ernest Willington Skeats, D.SC., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, B.A., B.E., D.SC., Government Geologist, Geological Survey Office, Adelaide.
1931 *Robin John Tillyard, M.A., D.SC., SC.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
1933 Walter George Woolnough, D.SC., F.G.S., Department of the Interior, Canberra, F.C.T.
1934 *Edward Sydney Simpson, D.SC., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
1935 *George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
1936 Sir Douglas Mawson, KT., O.B.E., F.R.S., D.SC., B.E., University of Adelaide.
1937 J. T. Jutson, B.SC., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
1938 *Professor H. C. Richards, D.SC., The University of Queensland, Brisbane.
1939 *C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
1941 Professor Frederic Wood Jones, M.B., B.S., D.SC., F.R.S., Anatomy Department, University of Manchester, England.
1942 William Rowan Browne, D.SC., Reader in Geology, The University of Sydney, N.S.W.
1943 Walter Lawry Waterhouse, M.C., D.SC.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.SC , F.R.S., University of Melbourne, Carlton, Victoria.
1945 Professor William Noel Benson. B.A., D.SC., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.
1946 Black, J. M., A.L.S. (*honoris causa*), Adelaide, S.A.
1947 *Hubert Lyman Clark, A.B. D.SC., PH.D., Hancock Foundation, U.S.C., Los Angeles, California.
1948 Walkom, Arthur Bache, D.SC., Director, Australian Museum, Sydney.
1949 Rupp, Rev. H. Montague, 24 Kameruka-road, Northbridge.

AWARDS OF THE JAMES COOK MEDAL.

Bronze Medal.

Awarded annually for outstanding contributions to science and human welfare in and for the Southern Hemisphere.

1947 Smuts, Field-Marshal The Rt. Hon. J. C., P.C., C.H., K.C., D.T.D., LL.D., F.R.S., Chancellor, University of Capetown, South Africa.
1948 Houssay, Bernado A., Professor of Physiology, Instituto de Biologia y Medicina Experimental, Buenos Aires, Argentina.
1949 No award made.

AWARDS OF THE EDGEWORTH DAVID MEDAL.
Bronze Medal.

Awarded annually for Australian research workers under the age of thirty-five years, for work done mainly in Australia or its territories or contributing to the advancement of Australian Science.

1948 Giovanelli, R. G., M.Sc., Division of Physics, National Standards Laboratory, ⎫ Joint
      Sydney.   ⎬ Award.
      Ritchie, Ernest, M.Sc., University of Sydney, Sydney. ⎭

1949 Kiely, Temple B., D.Sc.Agr., Caroline-street, East Gosford.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.
Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled " The Aborigines of New South Wales."

1882 Andrew Ross, M.D., Molong, for paper entitled " Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal.

1884 W. E. Abbott, Wingen, for paper entitled " Water supply in the Interior of New South Wales."

1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled " The Tin deposits of New South Wales."

1887 Jonathan Seavor, F.G.S., Sydney, for paper entitled " Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled " The Anatomy and Life-history of Mollusca peculiar to Australia."

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled " List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled " The Australian Aborigines."

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled " The Microscopic Structure of Australian Rocks."

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled " The effect which settlement in Australia has produced upon Indigenous Vegetation."

1894 J. V. De Coque, Sydney, for paper entitled the " Timbers of New South Wales."

1894 R. H. Mathews, L.S., Parramatta, for paper entitled " The Aboriginal Rock Carvings and Paintings in New South Wales."

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled " The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."

1896 Rev. J. Milne Curran, Sydney, for paper entitled " The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

1948 Waterhouse, Walter L., M.S., D.Sc.Agr., D.I.C., F.L.S., Sydney, in recognition of his valuable contributions in the field of agricultural research.

1949 Elkin, Adolphus P., M.A., Ph.D., Sydney, in recognition of his valuable contributions to the field of Anthropological Science.

AWARDS OF THE WALTER BURFITT PRIZE.
Bronze Medal and Money Prize of £75.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past six years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.

1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

B

1938   Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
1941   Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
1944˙ Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.
1947   John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.
1931   Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
1933   W. J. Young, D.Sc., M.Sc., University of Melbourne.
1940   G. J. Burrows, B.Sc., University of Sydney.
1942   J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.
1944   F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.
1946   Briggs, L. H., D.Phil. (*Oxon.*), D.Sc. (*N.Z.*), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.
1948   Ian Lauder, M.Sc., Ph.D., University of Queensland, Brisbane.

Royal Society of New South Wales

REPORT OF THE COUNCIL FOR THE YEAR ENDING 31st MARCH, 1950.

PRESENTED AT THE ANNUAL GENERAL MEETING OF THE SOCIETY, 5TH APRIL, 1950

(RULE XXVI).

The membership of the Society at the end of the period under review stood at 361, an increase of seven. Twenty-nine new members were elected during the year. However, 13 members were lost by resignation, and three, who were in arrears with subscriptions, were removed from the register. Six members have been lost to the Society by death since 1st April, 1949 :

Henry Harvey Dare (1890).
Walter John Enright (1916).
Joseph Foreman (1879).
Robert Thomas McKay (1891).
Dansie Thomas Sawkins (1941).
Charles Josiah White (1909).

Professor Sir Howard Florey, M.B., B.S., B.Sc., M.A., Ph.D., F.R.S., and Professor F. M. Burnet, M.S., Ph.D., F.R.S., were elected to honorary membership of the Society at the annual meeting on 6th April, 1949.

During the year eight General Monthly Meetings were held, at which the average attendance was 39. Forty-four papers were accepted for reading and publication by the Society—an increase of five from the previous year.

It has been the policy of Council to favour a broadening of the scope of the General Meetings and to encourage members other than the authors of papers to play an active part. In pursuance of this policy a portion of the time at general meetings has been devoted to " Notes, Exhibits and Questions ".

During the year the following questions have been answered :

4th May :

" Why do stars twinkle and planets not ? ", by Professor O. U. Vonwiller.

1st June :

" When a number is raised to the fifth power, why is the figure in the units place the same as in the original number ? ", by Dr. R. L. Aston.

7th December :

" How are earthquakes located at a distance ? ", by Rev. D. J. K. O'Connell.

On the 7th September, also, the following exhibit was discussed :

" Crystal of Synthetic Rutile ", by Dr. D. P. Mellor.

At the meeting held on 2nd November, the President announced that the Council of the Society had felt that there was need to organise an activity which would give members and their friends a better chance to meet and talk with one another than was possible at the ordinary formal meetings, and he welcomed members and their friends to the Conversazione.

The evening was devoted to Exhibits and Films of Scientific Interest. and this arrangement had been made possible through the courtesy of the following :

Australian Museum,
Department of Agriculture,
Museum of Technology and Applied Science,
National Standards Laboratory.
Sydney Technical College,
University of Sydney :
    Chemistry Department, and
    Geology Department.

At the meeting held on 1st June the following addresses were given :

" Notes on a Recent Journey to Europe ", by Professor O. U. Vonwiller.

" Visits to Observatories in Europe and America ", by Rev. D. J. K. O'Connell.

As has become customary, one meeting was devoted to the commemoration of great scientists. This meeting was held on 7th September, and at it the following addresses were given :

"Goethe's Work and its Significance in the Twentieth Century", by Professor R. B. Farrell.

"Edward Jenner and Vaccination", by Professor E. Ford.

"Life and Works of Pierre-Simon de Laplace", by Mr. H. H. Thorne.

Lecturettes given during the year were as follows :

3rd August :

"The Response of Marsupials to Pathogens", by Dr. A. Bolliger.

"Wolf's Creek Meteorite Crater", by Mr. R. O. Chalmers.

Five Popular Science Lectures were delivered during the year and were appreciated by members of the Society and the public :

19th May : "The Study of Earthquakes", by Professor K. E. Bullen.

18th August : "Radio Astronomy", by Mr. J. G. Bolton.

15th September : "Sex Control in Animals", by Dr. C. W. Emmens.

20th October : "The Australian and American Arnhem Land Expedition of 1948", by Mr. F. D. McCarthy.

17th November : "War Surgery through the Ages", by Dr. N. R. Wyndham.

The Annual Dinner of the Society was held at the Sydney University Union on 30th March, 1950. There were present 89 members and friends.

The Section of Geology, whose Chairman was Dr. G. D. Osborne, and Honorary Secretary Mr. N. C. Stevens, held five meetings during the year, at which the average attendance was 15 members and seven visitors. The activities were :

29th April : Address by Dr. G. D. Osborne and Mr. J. S. Proud, entitled "Occurrence and Probable Genesis of Asbestos at Wood's Reef, near Barraba, N.S.W."

20th May : Discussion on "The Geology and Mineral Resources of Tasmania", led by Dr. W. R. Browne. Mr. R. O. Chalmers showed exhibits from mining centres of western Tasmania.

16th September : Address by Dr. L. E. Koch entitled "On Pyrophyllite, its Mineralogy, Minerogeny and Economic Prospects in Australia". The address was accompanied by an exhibit of specimens.

21st October : Address by Mr. N. C. Stevens entitled "The Geology of the Canowindra District, N.S.W."

18th November : Notes and Exhibits by Miss F. Quodling, Mr. F. N. Hanlon, Mr. H. O. Fletcher, Mr. R. O. Chalmers, Dr. D. Carroll, Dr. L. E. Koch, Mr. T. G. Vallance, Mr. W. H. Williamson, Mr. N. C. Stevens and Dr. G. D. Osborne.

The Council of the Society held twelve ordinary meetings during the year, at which the average attendance was 13.

On Science House Management Committee the Society was represented by Messrs. H. O. Fletcher and F. R. Morrison, with substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

On Science House Extension Committee the Society was represented by Drs. A. Bolliger and R. L. Aston.

The Clarke Memorial Lecture for 1949 was delivered by Dr. W. R. Browne on 16th June, the title being "Metallogenetic Epochs and Ore Regions in Australia".

The Clarke Memorial Medal for 1950 was awarded to Dr. Ian Murray Mackerras, Director, Queensland Institute of Medical Research, Brisbane, in recognition of his distinguished work on Diptera of the Australian region.

The Medal of the Royal Society of New South Wales for 1949 was awarded to Professor A. P. Elkin in recognition of his valuable contributions to the field of Anthropological Science.

The Edgeworth David Medal for 1949 was awarded to Dr. Temple Bayliss Kiely for his research work in Plant Pathology.

The James Cook Medal was not awarded for the year 1949.

During the year several scientists from overseas visited the Society's rooms and were entertained by the President and Council. Among these were :

Sir Geoffrey I. Taylor, M.C., F.R.S., Fellow of Trinity College, Cambridge, and Yarrow Research Professor of the Royal Society. (11th May, 1949.)

Professor H. S. W. Massey, F.R.S., Goldsmid Professor of Mathematics at University College, University of London. (26th September, 1949.)

Dr. G. M. Lees, M.C., D.F.C., of the Anglo-Iranian Oil Co. Ltd. Dr. Lee was accompanied by Dr. Davies. (9th December, 1949.)

During his visit to Sydney, Dr. Lees delivered a lecture entitled " The Oilfields in the Middle East ". The lecture, which was given under the auspices of the Royal Society of New South Wales and the University of Sydney, was given on 9th December, 1949.

On 12th January, 1950, the Society arranged a public lecture by Professor Sidney Chapman, Sedleian Professor of Natural Philosophy at the University of Oxford. The subject was " Aurorae ".

The first Pollock Memorial Lecture, sponsored by the University of Sydney and the Royal Society of New South Wales, was delivered by Professor T. M. Cherry of the University of Melbourne, on 28th October, 1949. The subject of the lecture was " The Flow of Gases ".

The financial position of the Society, as disclosed by the annual audit, is not a satisfactory one.

The greatest single increase in the Society's expenses has been that of printing. The cost of production of the Society's Journal has increased from £12 per 16 pages, 1940, to £2 per page in 1950, and is still increasing. This, together with a steady increase in the number of papers accepted for publication, has meant that the Journal is now by far the costliest item on the balance sheet. The Council is fully alive to the threat to the Society's finances implicit in these trends, and desires to place the position clearly before members. Council believes that any curtailment in the publication of meritorious papers purely on the grounds of cost would be a retrograde step.

The scientific standing of the Society is linked with the quality of the papers published in its Journal. On the other hand, consideration of present costs makes it imperative for the Editor to impress upon authors the need for the utmost conciseness in expression. Council has found it necessary on several occasions this year to return papers to authors with a request for abbreviation. However, there is a limit to the extent to which any subject matter can be abbreviated and still remain intelligible, and a major subject for the deliberation of the incoming Council will be concerned with ways and means of meeting the rising cost of publication.

The Society's share of the profits from Science House for the year was £400.

The grant from the Government of New South Wales of £400 has been received. The continued interest of the Government in the work of the Society is much appreciated.

Original Manuscripts, Maps, etc.—At its meeting held on 27th July, 1949, Council decided that manuscripts, maps, etc., be made available to authors six months after publication.

The Library.—The amount of £38 4s. 8d. has been spent on the purchase of periodicals and £57 11s. 6d. on binding.

Exchange of publications is maintained with 399 societies and institutions, an increase of 12 over the previous year.

The number of accessions entered in the catalogue during the year ended 28th February, 1950, was 3,060 parts of periodicals.

The number of books, periodicals, etc., borrowed by members, institutions and accredited readers was 346.

The Society sold a number of bound volumes of early editions of *The Sydney Morning Herald* to the Library Board of Queensland for the sum of £86 10s.

Among the institutions which made use of the library through the inter-library borrowing scheme were : Australian Paper Manufacturers, Bureau of Mineral Resources, Colonial Sugar Refining Co. Ltd., Commonwealth Observatory, C.S.I.R.O., National Standards Laboratory, Division of Fisheries, Division of Food Preservation, Division of Industrial Chemistry, Division of Tribophysics, Elliotts and Australian Drugs, Forestry Commission, Melbourne University, M.W.S. and D. Board, New England University College, N.S.W. Department of Agriculture, Division of Wood Technology, Plant Research Laboratory, Public Library, N.S.W., Public Library, South Australia, Standards Association of Australia, Sydney Hospital, Sydney Technical College, Sydney University, Taubman's Ltd., University of Western Australia, Zinc Corporation.

<div align="right">HARLEY WOOD,
President.</div>

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1950.

LIABILITIES.

1949. £		1950. £ s. d.	£ s. d.
141	Accrued Expenses		470 6 0
26	Subscriptions Paid in Advance		33 1 6
90	Life Members' Subscriptions — Amount carried forward		107 5 0
	Trust and Monograph Capital Funds (detailed below)—		
	Clarke Memorial	1,957 1 1	
	Walter Burfitt Prize	1,090 12 5	
	Liversidge Bequest	733 5 3	
7,245	Monograph Capital Fund	3,620 3 4	
			7,401 2 1
26,082	ACCUMULATED FUNDS		25,579 11 3
	Contingent Liability—In connection with perpetual leases.		
£33,584			£33,591 5 10

ASSETS.

1949. £		1950. £ s. d.	£ s. d.
440	Cash at Bank and in Hand		403 1 6
	Investments — Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—		
	Held for—		
	Clarke Memorial Fund	1,800 0 0	
	Walter Burfitt Prize Fund	1,000 0 0	
	Liversidge Bequest	700 0 0	
	Monograph Capital Fund	3,000 0 0	
	General Purposes	4,660 0 0	
11,160			11,160 0 0
24	Prepayment		—
	Debtors for Subscriptions	57 17 0	
—	*Deduct* Reserve for Bad Debts	57 17 0	
14,746	Science House—One-third Capital Cost		14,835 4 4
6,800	Library—At Valuation		6,800 0 0
379	Furniture—At Cost—*less* Depreciation		360 0 0
27	Pictures—At Cost—*less* Depreciation		26 0 0
8	Lantern—At Cost—*less* Depreciation		7 0 0
£33,584			£33,591 5 10

TRUST AND MONOGRAPH CAPITAL FUNDS.

	Clarke Memorial.			Walter Burfitt Prize.			Liversidge Bequest.			Monograph Capital Fund.		
	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
Capital at 28th February, 1949 ..	1,800	0	0	1,000	0	0	700	0	0	3,000	0	0
Revenue—												
Balance at 28th February, 1949	160	4	7	55	17	5	7	10	3	520	18	4
Interest for twelve months ..	64	14	0	34	15	0	25	15	0	99	5	0
	224	18	7	90	12	5	33	5	3	620	3	4
Deduct Expenditure	67	17	6	—			—			—		
Balance at 28th February, 1950 ..	£157	1	1	£90	12	5	£33	5	3	£620	3	4

ACCUMULATED FUNDS.

				£	s.	d.
Balance at 28th February, 1949				26,081	18	2
Add Decrease in reserve for bad debts				27	8	0
				£26,109	6	2
Less—						
Deficit for twelve months (as shown by Income and Expenditure Account)	£436	3	7			
Amount written off *re* James Cook and Edgeworth David Medals..	71	10	4			
Bad Debts written off	22	1	0			
				529	14	11
				£25,579	11	3

The above Balance Sheet has been prepared from the Books of Account, Accounts and Vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1950, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

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HORLEY & HORLEY,
Public Accountants.

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Prudential Building,
39 Martin Place,
Sydney, 20th March, 1950.

INCOME AND EXPENDITURE ACCOUNT.
1st March, 1949, to 28th February, 1950.

1948-9. £		1949-50. £ s. d.	£ s. d.
640	To Printing and Binding Journal—Vol. 82	1,001 19 0	
468	„ Salaries	520 0 11	
133	„ Library—Purchases and Binding	113 4 8	
103	„ Printing—General	101 12 0	
97	„ Miscellaneous	68 2 2	
74	„ Postage and Telegrams	57 14 2	
55	„ Rent—Science House Management Committee ..	54 1 11	
—	„ Entertainment Expenses	16 8 11	
37	„ Cleaning	36 0 0	
23	„ Depreciation	21 4 0	
22	„ Telephone	14 11 11	
23	„ Insurance	23 13 5	
19	„ Audit..	18· 18 0	
9	„ Electricity	4 17 6	
2	„ Repairs	12 18 6	
	„ Reprints—		
	Expenditure £104 0 6		
	Less Received 81 1 3		
56		22 19 3	
	„ Annual Dinner—		
	Expenditure £88 4 4		
	Less Received 69 14 9		
39		18 9 7	
1,800			2,106 15 11
228	„ Surplus for Twelve Months		—
£2,028			£2,106 15 11

1948-9. £		1949-50. £ s. d.
586	By Membership Subscriptions	599 0 6
400	„ Government Subsidy	400 0 0
391	„ Science House—Share of Surplus	400 0 0
156	„ Interest on General Investments	161 13 2
478	„ Proceeds Sale of Old Library Books	89 17 8
5	„ Other Receipts	11 1 0
12	„ Proportion of Life Members' Subscriptions	9 0 0
2,028		1,670 12 4
—	„ Deficit for Twelve Months	436 3 7
£2,028		£2,106 15 11

Obituary

HENRY HARVEY DARE, a member of this Society since 1890, was born at Goulburn on August 25th, 1867, and died at Sydney on August 20th, 1949. He was educated at Sydney Grammar School and Sydney University, where he graduated as Bachelor of Engineering in 1888 and Master of Engineering in 1894, having been awarded a University Medal with each degree. After a short period on the staff of Sydney Observatory he entered, in 1895, the Public Works Department of New South Wales. He was responsible for the design of many public works. His last position with the Public Works Department was that of Chief Engineer for National Works and Drainage. When the Water Conservation and Irrigation Commission was constituted in 1913, he was appointed Chief Engineer to the Commission, and in 1915 Engineering Commissioner. He retired at the end of 1934.

The completion of Burrinjuck Dam, the construction of Wyangala Dam, works on the Murrumbidgee Irrigation Area and the establishment of Coomealla Irrigation Area, as well as the investigations of many of the proposals for water conservation throughout the State, were carried on under his direction. These have had a large influence on the development of Australian rural areas.

He was the New South Wales representative of the River Murray Commission from its inception in 1917 and a consultant on many major water supply works throughout Australia and New Zealand.

He was a member of a board appointed in 1918 to enquire into the extension of the water supply for Sydney, which recommended the construction of the Cordeau, Avon and Nepean Dams. The increase in average daily water consumption in Sydney from 41 million gallons in 1918 to 131 million gallons at present is sufficient to show the magnitude of the works in which he played an important part.

Mr. Dare was of retiring disposition and was held in high respect and esteem by all who knew him, especially by the staff who came under his control. He took an active part in the affairs of the professional bodies to which he belonged, and was a member of the Council of The Institution of Engineers of Australia, which awarded him the Peter Nicol Russell Medal. His death terminates the career of one of Australia's outstanding civil engineers.

WALTER JOHN ENRIGHT, who died on September 27th, 1949, was born on March 10th, 1874, at West Maitland, N.S.W. After two years in his father's auctioneering business he entered the legal profession, and graduated B.A. in 1893. It was while pursuing his University studies that he came under the influence of Professor David, being in one of the latter's first geology classes in the early nineties. The impress of Professor David on Enright's life was indelible, and although he was a very successful lawyer, becoming known throughout the Hunter River Valley, he never lost his love for geology, and indeed for many branches of natural history.

He was an amateur scientist of distinctly high calibre. His observations in various fields of natural science were accepted by professional scientists, and he was constantly appealed to by those seeking information about local geology, entomology, forestry, ichthyology and anthropology.

He wrote several useful original articles on some of these branches of science, and was instrumental in promoting research in many areas by assisting the work of the pioneers in various parts of the State, but particularly in the Hunter-Manning regions. His great energy, wide knowledge, tact and public spirit led to his assuming a leading place in his community, and he was actively associated with many worthy causes, especially with scientific and educational conferences or expeditions that were arranged in the northern part of the State. He played a dominant rôle in the whole organization of the visit to the Maitland district of Section C of the British Association in 1914.

He travelled widely in Australia and in the South-west Pacific, and his journeyings were always fruitful in scientific observations and in collection of exhibits.

Walter Enright will perhaps be best remembered by a host of friends of all classes because of his unfailing generosity and characteristic readiness to offer his services for any purpose to facilitate the work and promote the happiness of others.

He was elected a member of this Society in 1916.

ROBERT THOMAS McKAY was born on December 31st, 1865, and died August 10th, 1949. He had a distinguished career as a civil engineer and administrator of engineering projects. After a period of training he qualified under the Mining Act of New South Wales and was appointed surveyor of the Engineering Branch of the Department of Public Works, New South Wales. From 1896 to 1902 he was Resident Engineer of the Sydney and Suburbs Sewerage Scheme

and he was responsible for a number of important works carried out during his term of office. He was principal officer of the Interstate Royal Commission on the Murray River (1902–1903) to enquire into the allotment of waters as between New South Wales, Victoria and South Australia for the purposes of water conservation, irrigation and navigation, and the report of this Commission has served as a basis for the many negotiations which have taken place since on this important problem. His expert knowledge in this matter was recognized by an invitation to address a Premier's Conference. He made a special study of riparian rights, the control of water by the Crown and the supply and distribution of artesian water.

From 1905 till 1911 he was Engineer and Executive Member of Water Conservation, Irrigation and Drainage Board, and was associated with many irrigation projects throughout the State, particularly on the Murray, Lachlan and Murrumbidgee Irrigation schemes. He was subsequently Chief Assistant Hydraulic Engineer for the State of Queensland and later Chief Engineer for the Geelong Water Works and Sewerage Trust and Engineer for Wheat Storage in connection with the bulk handling of wheat. His final important public post was that of Engineering Member and Deputy President of the Sydney Harbour Trust from 1922 to 1930.

He was an advocate for using the waters of the Snowy River to supplement the flow of the Murrumbidgee and to provide a supply to Sydney. He was one of the earliest pupils of Sydney High School and throughout his life took a great interest in the school, being very active in assisting its advancement, particularly at the time when its new buildings were erected at Moore Park. After his retirement from the Sydney Harbour Trust he undertook private practice as a consulting engineer. He was a member of the Council of the Advisory Committee of the Institution of Civil Engineers for many years and occupied the position of Chairman of the Council for six years.

He had been a member of the Royal Society of New South Wales since 1891.

JOSEPH FOREMAN was born on August 23rd, 1852, at Pemberton, near Wigan, in Lancashire, England, and was trained in his father's profession of medicine at Edinburgh and at London, qualifying as a surgeon at Guy's Hospital in 1873.

He then became Medical Officer on S.S. *Bonny*, conveying troops to Sierra Leone to the Ashanti War, and in the following year was appointed Medical Superintendent on the ship *Baron Aberdare*, taking some hundreds of immigrants to Auckland, New Zealand.

He stayed in New Zealand as Medical Officer at Waimate, in the Bay of Islands, from August, 1875, until 1877, when he came to New South Wales, and for the next two years he practised in the Richmond River district.

In 1879 he set up in practice in Sydney and became interested in various medical, cultural and industrial societies, including this Society.

He was appointed Surgeon on the Medical Staff of the N.S.W. Volunteer Forces in 1881. Later in the same year he visited Europe, where he studied under the famous Berlin surgeon, Augustus Martin, and also obtained further experience at the London Hospital for Women.

On his return he became Sydney's first specialist in obstetrics and gynæcology and was appointed Honorary Surgeon at the Royal Prince Alfred Hospital, retaining his association with that institution until his death. He was also on the Honorary Staff of the Royal Hospital for Women, and Lecturer on Diseases of Women in the University of Sydney until 1920. Students who attended his lectures recall his precise, calm and dignified manner and his stress on meticulous cleanliness, tidiness and punctuality.

Besides achieving eminence in his chosen profession, he had an interest in farming and on his retirement from active medical practice, when over 70 years of age, he invested in pastoral properties at Cooma, Condobolin and Meadow Flat, near Bathurst. In 1948 the proceeds of the sale of some of these properties (£20,000) were devoted to the foundation of fellowships in connection with Royal Prince Alfred Hospital.

At the time of his death on January 15th, 1950, Dr. Foreman was the oldest member of this Society, having been elected in 1879.

CHARLES JOSIAH WHITE, a member of this Society since 1909, was born in 1881 at Wollongong, N.S.W., and received his early education at Wollongong.

He began his life-work in the teaching profession as a pupil-teacher at Gerringong and later at Wollongong. In 1902 he entered the Teachers' Training College at Fort Street Model School. After a distinguished undergraduate career in the University of Sydney, he graduated Bachelor of Science in 1907 with the University Medal for Chemistry, of which he was the first recipient, and Bachelor of Arts in 1908.

On the completion of his University course he was appointed Lecturer-in-Charge of Science at the Teachers' Training College, Sydney, and in this position he exercised a great influence on the teaching of science in the secondary schools of New South Wales until his retirement in 1945.

He died on July 31st, 1949.

DANSIE THOMAS SAWKINS, a member of this Society since 1941, was born on August 1st, 1880, at Muswellbrook, N.S.W., and died on March 22nd, 1950.

After his early education at Maitland he graduated from Sydney University as Bachelor of Arts with the University Medal for Mathematics in 1899, and Master of Arts in 1902. As James King of Irrawang Travelling Scholar he went to Cambridge, England, and graduated a Wrangler in 1904.

From 1904 to 1907 he was a schoolmaster in England; he then went to Siam and the Federated Malay States as a surveyor for five years, and on his return to New South Wales he worked as a surveyor in the State service for about five years.

Between 1917 and 1938 he was Statist to the Board of Trade and the Industrial Commission. He became Lecturer in Statistics at the University of Sydney in 1922 and in 1924 was appointed Peter Nicol Russell Lecturer in Geodesy. In 1938 he joined the full-time staff of the University of Sydney as Reader in Statistics.

He published a large number of papers on various aspects of statistics both in Australia and abroad, three of which appear in the *Journal and Proceedings* of this Society.

PRESIDENTIAL ADDRESS

By Harley Wood, M.Sc.

THE WORK OF THE SOCIETY.

The Annual Report of our Society indicates a year of useful activity. The usual monthly meetings were held, except for the one in July, which was cancelled owing to power restrictions. In August an afternoon meeting was held in the Geology Lecture Theatre at the University. The meetings of May, June, October and December were devoted mainly to the presentation of original papers and to lecturettes in the form of answers to questions brought forward by members. At the August meeting we had two lectures by members of the Council; the September meeting commemorated the centenaries of Goethe, Jenner and Laplace, and the November meeting took the form of a conversazione, at which there were films and exhibits of scientific interest. Sitting, as I have done as your President, on the dais in front of the meeting, I have not been able to avoid noticing that the number of members who attend varies as the amount of material of general interest on our agenda. When we have devoted our attention entirely to the presentation and discussion of original papers, the audience has been just comfortably over the number we need for a quorum, whereas at the September and, especially, the November meetings our hall was well filled. In this respect the introduction into our meetings of questions by members has certainly proved a satisfactory way of finding interesting topics and speakers who might not otherwise have come forward. Naturally, many authors who present papers to the Society are anxious to have them discussed at a meeting, but, in view of experience while I have been in the chair, and indeed, observation for some years past, I believe that all such presentations should be as nearly popular as possible. In most cases our audience can only have a very few specialists in the subject of a paper, and it is necessary for authors to speak more at the level of the unsophisticated majority. It should usually be possible to explain the background of a piece of research in such a way that most of us can understand the kind of contribution which is being made.

The Clarke Memorial Lecture for 1949 was delivered by Dr. W. R. Browne, who spoke on " Metallogenetic Epochs and Ore Regions in Australia ". During the year there were five popular science lectures. All of these produced satisfactory audiences and, in three cases, the hall was full to overflowing.

Two years ago the Council of the Society decided to institute a series of monographs, and this year the first one to be accepted was presented by Dr. G. D. Osborne. It is entitled " The Structural Evolution of the Hunter-Manning-Myall Province ".

It is my pleasant duty to thank the members of the Council, and indeed the general membership of the Society, for the cooperation I have received during the year and for their goodwill, which has made it a pleasure to preside at our meetings. My thanks are due especially to the Honorary Executives who have carried on the work with such devotion. Dr. Bosworth has kept able hands on the management of the Society's affairs. Mr. Smith-White, as editor, Dr. Bolliger as treasurer and Mr. Hanlon as librarian have given without stint time, energy, and in each case more than ordinary skill.

We live in an age when man is bewildered by his own technical achievement. Science has placed in his hands a power altogether beyond the dreams of our forefathers—a power that may be used for good or for destruction. The atomic physicist has already demonstrated the destructiveness of his contribution, but has only just begun to tame his monster so that it may be used for the service of society. The biological scientist, not to be outdone, insists that he has weapons available which can strike a blow no less terrible than the atomic bomb.

The questions posed by the enhanced possibilities for purposive destruction, important as they are, represent only a part of the problem that is being thrust on mankind. We have seen more clearly than ever before that, in a few generations, man can use up the resources of power which nature in past ages has gathered from the sun and stored beneath our soil. We know that a few generations of misuse can so reduce the fertility of that soil that the precarious existence we now wring from it, and we must not forget that for the bulk of mankind it is precarious, will be endangered.

The suggestion is often made that certain weapons of war should be outlawed ; but war is the negation of law and it is not conceivable that a nation would allow itself to be defeated, leaving unused a weapon which might bring victory. According to recent press reports, Einstein has stated his belief, and I think he is right, that the real alternative is that the political leaders of the world will be deterred from war for a period long enough for the world to evolve some sort of central government. In the past, the tendency has been for larger groups of mankind to be formed by the amalgamation of smaller ones. One group might conquer its neighbour, or combine with it through the fear of a third power, and throughout history the powerful interest that has compelled loyalty of different groups to common leaders, has been the threat of some external aggressor. Now that the enemy is recognized to be war itself, surely we can feel and foster a loyalty to mankind as a whole.

Science now has prestige, responsibilities and, especially, dangers that it had not before. The characteristic of science is that every hypothesis should undergo the searching test of discussion and comparison with observation, and we have come to realize that, even such larger advances as the invention of the quantum theory are only scaffoldings on which to unify the knowledge already gained before proceeding to build further. Science distinguishes real advances, which provide tests to which observation can be directed and to which they stand up, from those which cannot be applied in a way which will test their truth, and it implies a complete freedom of thought and of criticism, and the display for criticism of all ideas within the realm of human knowledge. It is by such means that knowledge advances. Now the advancement of knowledge and the greater dissemination of it are essential if humanity is to be freed from the chains placed upon it by want and fear. We all know that the power over nature he now wields has produced a tendency to place restrictions on the scientist and on free interplay of scientific discussion and criticism. This applies in almost all countries of the world at present, and most members will be able to recall cases of men of science having their activities restrained in some way or other. Well publicized examples of interference with the freedom of science have occurred in many countries. A characteristic of this age is its science and technology, and one phase of this is that many of the most alert and able minds of the time are being attracted to science. One can observe signs that, if science were to lose that freedom in which such alertness can flourish, it would begin to wither for want of support. It has been freely stated that, despite advantages offered in the way of opportunity for research and in the way of equipment of the very best kind, the best scientists are not attracted to government laboratories dealing with the development of weapons of war ; and if the attitude

of the community becomes further unfavourable to the work of science there will be little attractiveness left in it.

In such a background our Society has an opportunity and a duty to provide a forum for the discussion among scientists of matters of general interest which affect them in their professional work. An example of this sort of discussion was the symposium on " The Education of a Scientist ", which we held in 1948 and which aroused considerable interest, but I believe that we should occasionally have discussions on more controversial, and probably more vital, matters. On the other hand we need to foster the penetration of the scientific outlook into our Australian community and, while we now do this in some degree by our popular science lectures, it will be readily admitted that there is a great need for work which is more explicitly directed towards improving the prestige of science.

Wherever I have been as your representative I have found our Society held in high esteem. It is the only society in New South Wales which unites all of the sciences ; other organizations are limited to one science or group of sciences or by being professional associations, whose proper care is for the status of their members.

Of the various organizations to which I have belonged this is the one of whose usefulness I feel most convinced and the association with which affords me most satisfaction.

We must continue our work despite the difficulty of the times, indeed, in some respects, because of it. We must endeavour more consciously, on the one hand, to foster public interest in science and to make known the value of science and scientific research in the economy and in the culture of our country and, on the other hand, to provide more and more a meeting-ground for the various specialist sciences and for the scientists who practise them.

ASTRONOMY IN AUSTRALIA.

THE HISTORY OF ASTRONOMY IN AUSTRALIA.

Astronomy was closely associated with the beginning of British settlement in Australia. The idea of using the observation of a transit of Venus to determine the distance of the Sun was first suggested by Kepler, and again with more practical detail by Halley in his report of the observation of a transit of Mercury, which he saw at St. Helena in 1677 and published with his Catalogue of Southern Stars. It was important that this constant, the fundamental unit of the Solar System, should be determined with all practicable accuracy and the scientific world was anxious to make use of the transits of Venus in the eighteenth century, sending on each occasion expeditions to distant parts of the world. For this reason James Cook was despatched to Tahiti to make observations there. The transit was observed on April 13, 1769, and the published results (Green and Cook, 1771) although not as precise as had been hoped, because of unexpected observational difficulties, nevertheless did yield an improved value of the solar parallax.

On this scientific expedition Cook made the exploration of the east coast of Australia which led to the foundation of the colony in 1788. With Captain Phillips' first fleet, too, there was an astronomer, Second Lieutenant William Dawes. One of his duties was to establish a post from which he was to attempt to observe the expected return of a comet.

Among the comets which had been discussed by Halley were two observed in 1532 by Appian and in 1661 by Hevelius. Having calculated that they had similar orbits, Halley conjectured that they were identical and that a new return would occur about 1790. This was discussed by Maskelyne (1786). The anxiety to observe this object was quite natural because at this stage the only

predicted return of a comet which had been verified was the famous one of Halley, and the only other body added by observation to the classical members of the Solar System was the planet Uranus. Several writers who refer to this matter mention that Dawes made no observation of this comet, and indeed, that no purely scientific observations were known to be produced from his observatory. They do not appear to add, however, that this is quite natural, since the comet was also not observed in the northern hemisphere where it should have been seen to better advantage, although at a later stage. In any case, Halley's conjecture was probably wrong, as the observations of the earlier comet are from the viewpoint of orbit computation not satisfactory, and computers differ a good deal as to the real character of the orbit of the comet of 1532. Dawes, too, could scarcely have been expected to undertake other astronomical work since, as well as being charged with the care of a small garrison, he was a very active member in the survey and exploration of the young colony. Besides other maps prepared later, he made a sketch of an area of the southern shore of Sydney Harbour as early as July 1788, on which his observatory is marked, its position being noted as longitude 151° 19′ 30″ and latitude −33° 52′ 30″.

When Sir Thomas Brisbane was appointed Governor of New South Wales the British Government had already decided to establish an observatory at the Cape of Good Hope and so there was no opportunity for him to persuade his government to establish with public funds another observatory in the southern hemisphere. He determined himself to erect an observatory near to Government House in Parramatta. He arrived in Sydney in November 1821, and his instruments were set up in time to observe the solstice in December. His interest in the scientific culture of New South Wales is shown by the fact that before the end of 1821 he became president of the newly formed Philosophical Society of Australia, which was the predecessor of the Royal Society of New South Wales. The success of the work at Parramatta is shown by the fact that the three workers in the Parramatta Observatory, Brisbane himself, Dunlop and Rumker, all received the Gold Medal of the Royal Astronomical Society. One important piece of work done at Parramatta Observatory was the observation of Encke's Comet on its first predicted return in 1822. This was only the second case of a predicted return of a comet being verified, although several other comets had periodic orbits attributed to them by this time. After Brisbane's departure Parramatta Observatory was carried on, first by Rumker and then by Dunlop, but was finally closed in 1847.

Sir William Denison became Governor General in 1855, having previously been Governor of Van Diemen's Land, and it was due to his representation that the present Observatory was established. William Scott was appointed on the recommendation of the Astronomer Royal and arrived in Sydney in November 1856. The present building was started in 1857 and observations commenced in June 1858. Scott was honorary secretary of the Royal Society of New South Wales from 1867 to 1874 and honorary treasurer for several years. He joined in 1856 when it had newly assumed the title " Philosophical Society of New South Wales ", and was the oldest member of the Society before he died in 1917. Indeed, astronomy in New South Wales has always been closely associated with our Society, and besides the influence of Brisbane it may be mentioned that of the six directors of the Observatory five have held executive positions in the Society and four have been president or held office equivalent to the presidential status.

As its share of an international plan to catalogue the positions of stars to a faint magnitude over the whole sky, Sydney Observatory undertook responsibility for the zone between south declinations 51° and 65°. In recent years most of the work of the Observatory has been associated with this Astrographic Catalogue,

somewhat more than half of which is now published and in the preparation of which several meridian catalogues have been prepared. Sydney Observatory has also published work on double stars and occultations of stars by the Moon.

Williamstown Observatory was founded in 1853 when R. L. J. Ellery was appointed by the Government of Victoria but it was dismantled in 1863 and the instruments were moved to Melbourne. Among the instruments Melbourne Observatory acquired was an 8″ meridian circle installed in 1884 and the 48″ reflector installed in 1869. Melbourne Observatory was closed as a State institution by the Victorian Government in 1944. Several valuable catalogues of star places based on meridian observations were left and are being prepared for publication by the Commonwealth Observatory. It may be possible to make arrangements to complete at Sydney Observatory the Melbourne section of the Astrographic Catalogue from −64° to the South Pole. As comment on the closure of Melbourne Observatory, I would say that it has since been necessary to provide telescopic demonstrations for educational purposes and to carry on certain other services of the old Observatory, and so the financial saving made by the decision to close the Observatory by no means equals the whole of the expenditure which was formerly made on it.

In 1855 Charles (later Sir Charles) Todd was appointed Superintendent of Telegraphs and Astronomical Observer for the colony of South Australia; and in 1874 the Adelaide Observatory was erected and provided with instruments. It has issued a series of publications on Jupiter, carried on some meridian observations and maintained observations of variation of latitude, which are part of an international cooperative plan. Most of the Adelaide Observatory buildings have now been demolished to make room for a school and it is intended to make the University responsible for future astronomical work.

Perth Observatory was founded in 1896 when W. E. Cooke was appointed Government Astronomer for Western Australia. In 1900 Perth undertook a share of the Astrographic Catalogue between −31° and −41° and its published work consists of meridian catalogues associated with reference stars for this work, and various volumes of the Catalogue, most of which has been published.

Although we are discussing chiefly professional astronomy, no account of the subject in Australia would be complete without mention of John Tebbutt, who worked as an amateur from about 1854 until 1904, maintaining at Windsor an observatory which became known throughout the world. He made altogether over 350 contributions to scientific journals, largely observations of comets, minor planets and double stars. Astronomy has had many celebrated amateurs. If we exclude those who became and worked much as professionals, John Tebbutt would rank very high indeed among the contributors to astronomical science.

Two further astronomical observatories have been established in Australia in this century. Riverview College Observatory was established by the Society of Jesus as a seismological station in 1908, with Father E. F. Pigot as first director, and in 1931 began astronomical observations. Valuable contributions are being made to astronomy by this Observatory, particularly important being the study of variable stars of the southern skies.

After careful testing of conditions on Mt. Stromlo, a few miles west of the Australian capital at Canberra, it was decided to establish an observatory there and a staff was appointed which began work in Canberra in 1925 and observations on Mt. Stromlo in 1926. Thus was established the strongest astronomical institution that Australia has had. It was called the Common-wealth Solar Observatory, but has now been renamed the Commonwealth Observatory to correspond more with its wider purpose. In its comparatively short life it has become an important contributor to research in a widening field of astronomical endeavour. The 48″ telescope, formerly at Melbourne, is being modernized at Mt. Stromlo and soon a 74″ reflector will be working beside it.

ASTRONOMY AS AN OPPORTUNITY TO AUSTRALIAN SCIENCE.

For any country there are always subjects of research which represent a special obligation or, in some cases, a special opportunity. Thus unless we in Australia investigate the meteorology of our country and its natural resources, we will leave a gap in information which is important, not only for ourselves, but as part of a world picture. A president of our Society, in his address four years ago, pointed out that we are under an obligation to study Australia's marsupial fauna. For Australians there is a similar obligation to astronomy. The object of my address is to point this out and at the same time to show that northern astronomers planning work in the southern hemisphere should consider coming to Australia. Because the great bulk of the wealth and population of the world must always remain in the northern hemisphere and, because there are important parts of the heavens not visible from the latitudes of Europe, North America or Asia the countries of the southern hemisphere can make a contribution to astronomical science more than proportional to the resources used, when compared to the efforts of northern astronomers. The study of the structure of the star-system in which our Sun is situated, or of the organization of the systems of which ours is but one, is impeded if the knowledge of a large area of the sky is comparatively incomplete. There is ample evidence of the need for astronomical research in the southern hemisphere to be brought in line with that of the north, and of the great opportunities which exist this side of the equator in the fact that observatories of many northern countries have expensive branch observatories in southern foreign lands. By far the greatest power of equipment is in the northern hemisphere. Of reflecting telescopes equal to or exceeding 36″ in aperture, there are 27 in the world, of which four are in the southern hemisphere and only one in Australia. Of the refractors 24″ or more in aperture, there are 26 in the world, six in the southern hemisphere and none in Australia.

To indicate the ways in which Australia can contribute towards astronomical research, let us first list the objects of study towards the understanding of which research is directed. These are :

1. The structure of the Solar System ;

2. The physical constitution of members of the Solar System ;

3. The physics of the Sun, which, of course, might be included as a member of the Solar System or as a particular star, though the study of the Sun is so important that it deserves a heading of its own ;

4. The structure of the Galaxy and of other star systems ;

5. The physical constitution of individual objects in the Galaxy including, for example, stars and the gaseous nebulæ ;

6. The structure of the Universe.

Until the end of last century the emphasis in effort was mostly on the first two of these subjects ; but in this century the fourth and fifth have become of dominant importance, and it is likely that as time goes on the last one will advance beyond the pioneering stage and assume a greater place in the thoughts of the working astronomer. In the year books of the Carnegie Institution of Washington of almost fifty years ago concern was expressed at the lack of data on the southern skies as compared to those of the north, and ways of improving the situation were discussed. It was pointed out that the positions and proper motions of southern stars were required to facilitate the study of the motion of the Sun and the then newly discovered streaming of stars. (We now recognize other important systematic motions requiring study.) The important positional work done by the expedition to San Luis, the work of the Cape Observatory over a long period and the zone catalogues of the La Plata Observatory have improved this position very greatly and the data in the General Catalogue is not

yet fully discussed. However, it is necessary still to remember that observations must go on and that the resources of positional astronomy in the south remain below those of the northern hemisphere. At Sydney Observatory we are planning to continue positional work. By re-photography of the astrographic zones and comparison of the new plates with old ones, reliable proper motions should be obtainable ; we will be mounting a new specially designed photographic lens on the astrographic telescope. The pioneering stage is now over and only observations of the highest quality will make a useful contribution. Fifty years ago it was also pointed out that the southern hemisphere was seriously behind in observations of stellar parallax and of double stars, and in capacity to make such observations. This position has been largely improved by the work of the Cape Observatory, the Bosscha Observatory at Lembang, the Yale University Observatory station at Johannesburg, the Union Observatory, Johannesburg, and the Lamont-Hussey Observatory of the University of Michigan. It was remarked, too, that the knowledge of radial velocities of the southern objects was falling behind the knowledge of those of the northern hemisphere, and that photometry of the stars of the southern sky was very much needed ; and these deficiencies remain.

Among the most fundamental of the data required to study the galactic system are well determined magnitudes for the stars concerned. Careful observations have been made for a long time ; for example, William and John Herschell made determinations more than 100 years ago and so we would expect there to be a great body of reliable data ; but actually our knowledge of stellar magnitudes is much below the needs of astronomy and there is much work to be done in the northern hemisphere and the south is still very far behind. It is hard to imagine observational astronomy in a condition where there will not be a need for a substantial amount of photometric work on the stars. The apparently slow progress made in developing reliable stellar photometry is due to the difficulty of the observations which have to be made, and only gradually have the number and complexity of the systematic errors revealed themselves. At first, the photometry was done visually and astronomers relied upon the eye to integrate the visible light of the stars in making comparisons of brightness between them. A similar principle was used when photographic magnitudes became common, but the stars, being of different temperatures and having their energy distributed through their spectra in different ways, are affected differently by the atmosphere, by the instrument, by the method of observing, or the personality of the observer, and so gradually it became necessary to evolve a more precise definition of magnitude which did not involve the allowance for so many variables. In recent years, the emphasis has come to be on monochromatic photometry, where only a narrow range of the spectrum of the star is used and where we can rely upon the atmosphere and the instrument affecting the light in a similar way for different stars. This gradual improvement in photometric method means that for modern needs much of the work has to be revised ; indeed, in the southern hemisphere it has to be revised almost from the beginning. Work of this kind has been undertaken in observatories in South Africa and our own Commonwealth Observatory. There will be need for the magnitude-system to be extended to faint magnitudes, for the number of stars per square degree to various magnitude limits to be determined so that statistical methods may be applied to them in order to study the structure of the galaxy. The discovery and examination of transparent areas of the Milky Way is expected to yield important clues concerning its structure. By methods such as the study of the continuous spectrum of the stars at Greenwich, or as monochrometric photometry at different wave lengths at Mt. Wilson, the colours of the stars in the southern sky need to be studied to extend the work which has been done in the northern hemisphere. It will soon be necessary to follow

the northern workers into the infra-red region and it seems that the examination of continuous spectra of variable stars (particularly eclipsing ones) might yield some results of interest. This kind of work is valuable not only in studying the stars themselves but also in studying the inter-stellar material through which the light from the stars has to pass before it reaches us. Some of the light is absorbed by the material and the way in which it affects the colours of the stars has already taught us much about the distribution, density and nature of this material ; mostly, however, in northern hemisphere areas. Exploratory work on the spectrum lines arising from inter-stellar absorption is also much needed.

When we go beyond the galaxy there is need to find the total magnitudes of nebulæ in the southern hemisphere which are beyond the reach of the northern observers, and to determine isophotal lines and make detailed spectral and photometric examination of resolved objects, particularly variable stars. In this connection it should be remembered that the Magellanic Clouds are the nearest of the star systems which can be surveyed as a whole from the outside and the study of them by all the methods which may be available should yield results of importance, not only in studying these systems but also, more fundamentally, in increasing our knowledge of the way in which the star systems behave. Statistical data on their stars, having regard to magnitude, spectral class and position in the system, are needed together with values of stellar motions, based upon radial velocity measures, and possibly on proper motion measurements ; for, if stars of the Magellanic Clouds have high systematic motions, it might be possible for them to be measured, although, if the motions are not substantial they will be very difficult to disentangle from the systematic motions of reference objects among the stars of our own galaxy. In addition to the important and widely interesting topics I have already mentioned, it should be remembered that many other problems need to be studied over the whole sky and require observation from both hemispheres. For example, research on meteors is more advanced in the northern hemisphere than in the south in spite of the valuable work of an amateur group in the Royal Astronomical Society of New Zealand. Most of the work of observing minor planets can be done from the northern hemisphere but there is still a need for cooperation from southern observers in observing minor planets which culminate well south of the equator at opposition or when the effects of parallax have to be examined or eliminated. The new lens at Sydney will be suitable for this kind of observation.

So far the most important deficiencies in apparatus in the southern hemisphere have been in the direction of large astrophysical equipment. This will be partly offset now that the Radcliffe telescope of Oxford University has been put into commission in South Africa and the 74″ telescope at Mount Stromlo will be due in a few years.

Recently, the National Geographic Society (of America) and the California Institute of Technology have sponsored a project for mapping the whole of the accessible area of the heavens with the 48-inch Schmidt camera of Mount Palomar. Each section of the sky will be photographed once in red light and once in blue light. This will provide a survey which should uncover many interesting objects for detailed examination by the great reflectors and give important material for statistical work. There have been no Schmidt cameras in the southern hemisphere but this will be partly remedied now that the instrument operated by Harvard, Dunsink and Armagh Observatories is becoming available. Mount Stromlo, too, may adapt the 48″ telescope to carry a Schmidt camera. As at least one of these is to be fitted with an objective prism another southern hemisphere deficiency will have been mitigated. There is no telescope corresponding to the 20″ astrographic telescope at the Lick Observatory in the southern hemisphere ; nor, as far as I know, is there one projected. One of the purposes of this instrument was to refer the system of

stellar motions to the galaxies beyond our own and, unless the data becomes available for the southern part of the sky, this investigation might easily strike difficulties when the interpretation of the results is to be made.

One thing that must be remembered is that, although there are some men like Eddington and Russell whose powerful ideas enable them to contribute greatly to their science, nevertheless most of the important contributions to astronomy, such as the resolution of the nearer nebulæ into stars earlier in this century, come from workers with powerful equipment and the most valuable contribution that southern workers can make is by observation. We must therefore see that our observatories have adequate and up-to-date equipment.

On the Choice of Sites for Observatories.

Having established that opportunity is good for astronomical work in the southern hemisphere, we need to decide whether there are suitable places for it in Australia. Let us list the requirements.

1. The site should be satisfactory from the meteorological point of view, having a good proportion of clear sky, a low average wind velocity, and a low average daily temperature range. Strong winds tend to cause instruments to vibrate and lead to lack of homogeneity of the atmosphere from an optical point of view, and a large temperature-range causes expansion and contraction of instruments, which is particularly undesirable in large optical parts.

2. A site some miles away from big industrial plant, or from a situation where such plant could come, is preferable ; for example, a large deposit of iron or coal might prove a bad neighbour.

3. Adequate supplies of electricity and water and accessibility by road or rail transport would be necessary, since, if they were not available, provision of them would take too much of the resources of all but the most ambitious schemes.

4. Living conditions for staff should be good and this implies reasonable proximity to town and educational facilities ; this is now recognized as desirable, even if only scientific efficiency is taken into account.

5. The atmosphere at the site should have a standard of transparency which is high and constant relative to varying position in the sky or to time. This is necessary for almost any work, and particularly for photometry. The background sky brightness should be low for photography with fast instruments. The meteorological corona must be low for some work.

6. For work requiring good image quality, such as measuring double stars or examining planetary detail, the seeing conditions require to be of high average quality.

These are very stringent requirements and much trouble is often taken to discriminate between available sites. Of course, a lot of the work can be done at the desk by examining meteorological and other statistical records, but it is necessary, in particular cases, to make quantitative estimates in the field of quality of the atmosphere before establishing a large and expensive institution. Sometimes, of course, considerations other than purely scientific suitability have to be taken into account. An observatory associated with a university should be near enough to the university for students to do observational work without the handicap of too much travelling.

It is also desirable that the site should be at least some distance from the sea, since, according to Middleton (1941) sea salt nuclei, even in smaller numbers, are more effective in limiting visual range than dust or combustion nuclei. Moreover in eastern Australia the coastal areas are inferior from the point of view of freedom from cloud. Regarding seeing conditions, it seems established

that there can be deficiencies which are very localized, as well as wide regional characteristics, and it would be indeed unwise to establish an observatory at a place where the topography showed marked lack of symmetry, as by the sea shore or on the slopes of mountains. In such places frequent diurnal winds are likely to be destructive of good seeing. Places at which there is a strong frequency of wind coming from higher topography should also be avoided, unless they have been tested. The bad effect this has on seeing conditions has been noted at many places.

It is always considered desirable to situate observatories at a considerable height above sea level in order to have below the observer a good deal of the atmosphere, including the part which, being least transparent and most subject to turbulence, interferes most with good optical quality of the air. The actual site should be somewhat above the surrounding landscape, in order to lift it above the ground haze, and above any dust which might be raised with particles large enough to fall quickly in the air. Elevation above the surrounding landscape also reduces the diurnal range of temperature. Another advantage is that the air should tend to settle downwards on the top of a hill at night. This should bring the haze level down at night and the gradual settling of the air should be favourable to good seeing conditions. In regard to atmospheric pollution from towns : it is well to remember that the effect is carried a good many miles to the lee of its source, and situations, whose prevailing winds might carry such pollution towards them must be regarded as unfavourable. The situation of the observing site above the surrounding topography will be of value towards eliminating this effect. However, when selecting a site for daytime observation, it might be preferable to avoid a hilltop about which air might tend to rise and produce undesirable optical effects.

On both sides of the equator there are high pressure zones which should be, and indeed have been, found very favourable for astronomical observation. In these zones the incidence of cloud is much lower (Brooks, 1930) and frequent stability or slow settling conditions in the atmosphere favours good seeing.

At the 1948 meeting of the International Astronomical Union it was suggested that an international observatory should be established and located between 10° and 40° south latitude. The requirements for the sites suggested were that it should be noted for its fine seeing, preferably at an altitude of between 6,000 and 10,000 feet, with not less than 225 clear nights per year and no two-month period more than fifty per cent. cloudy. It was admitted that these specifications might be very hard to satisfy, and, although in Australia there would be excellent sites found, the altitude requirement would be a very restricting one. I am inclined to think that the value of an altitude above two to four thousand feet could easily be overrated, provided that tests of seeing and transparency gave satisfactory results. The absorption (photographic, see Buisson et al., 1930) caused by passage horizontally through 3,000 feet of the atmosphere at altitude 1,000 feet would be about 0·04 magnitude and this is a substantial proportion of the absorption at a good astronomical site where the extinction coefficient might be 0·15 mag., and the absorptive capacity of the atmosphere is much greater in its lower layers and varies rapidly with height (Middleton, 1941). It will be seen that only very large increases in altitude of the place will affect the result very materially after, say, 3,000 feet. Australia is very favourably situated in the southern hemisphere, having the largest part of its area in the latitude zone most likely to be favourable, and having large areas with good freedom from cloud. The northern limit for placing the observatory should be more like 25° south latitude, since any further north would place at too great a zenith distance the part of the sky which is most completely inaccessible to northern countries and which it is most essential to observe.

AUSTRALIAN METEOROLOGY FOR ASTRONOMICAL OBSERVATION.

We can now apply the considerations of the previous section to Australia. Figure 1 is a previously unpublished map of " Clear and Cloudy Days ", which is included by kind permission of the Director of Meteorological Services (of Australia). I have also to thank Mr. C. J. Wiesener of the Meteorological Bureau at Sydney for assistance with climatological material. It is divided into regions over which the cloud regime remains much the same. By a clear day is meant one which is judged to be equal to or less than two-tenths cloudy, and by a cloudy day one equal to or greater than eight-tenths cloudy. The number of
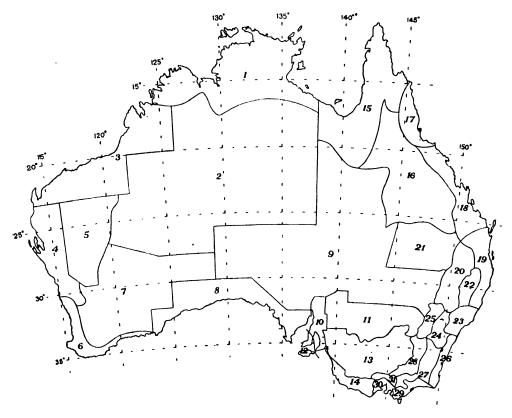
Fig. 1.—Clear and Cloudy Days in Australia.

clear days recorded in each quarter (the first including December, January and February) is given for each region in the first column and the number of cloudy days in the second (bracketed) column.

Another map which is sometimes used to find places which should be free from cloud is one showing the average annual number of days of rain. Such maps are available in a publication by the Meteorological Branch (1945) or by T. G. Taylor (1920). There are large areas in Australia which have less than 30 days of rain in the year but in the areas where living is congenial it might easily be necessary to be satisfied with 60 days. According to the data given by Brooks (1930) a location averaging four-tenths cloudy is a favourable one and, indeed, one as good as this is not likely to be found outside the zones of maximum pressure on either side of the equator. It may be mentioned that when places were being selected for the Harvard stations for observation of meteors it was

Region.	Quarter Dec., Jan., Feb.	Quarter Mar., Apr., May.	Quarter June, July, Aug.	Quarter Sept., Oct., Nov.
1	12 (31)	40 (15)	68 (5)	42 (6)
2	35 (12)	46 (10)	57 (7)	50 (5)
3	39 (7)	51 (12)	71 (7)	67 (3)
4	45 (5)	43 (9)	46 (9)	54 (6)
5	43 (8)	45 (10)	50 (11)	52 (4)
6	23 (15)	17 (28)	10 (30)	15 (23)
7	55 (10)	44 (16)	32 (25)	43 (17)
8	27 (14)	25 (17)	26 (15)	28 (15)
9	43 (10)	50 (8)	53 (9)	54 (7)
10	32 (12)	27 (17)	17 (19)	24 (16)
11	48 (11)	41 (12)	29 (15)	39 (12)
12	15 (18)	9 (22)	3 (27)	7 (23)
13	42 (8)	36 (14)	21 (22)	33 (16)
14	14 (21)	13 (25)	9 (27)	11 (25)
15	10 (19)	24 (9)	45 (7)	27 (4)
16	27 (16)	38 (11)	56 (9)	47 (5)
17	8 (19)	10 (14)	26 (10)	16 (5)
18	14 (13)	24 (11)	42 (10)	30 (5)
19	13 (17)	15 (18)	30 (18)	22 (16)
20	34 (13)	44 (12)	51 (14)	46 (9)
21	34 (10)	40 (7)	52 (13)	49 (10)
22	24 (17)	24 (18)	27 (19)	29 (10)
23	13 (17)	15 (17)	18 (14)	15 (15)
24	30 (18)	26 (27)	34 (18)	36 (17)
25	36 (8)	35 (8)	32 (16)	37 (11)
26	15 (23)	21 (22)	30 (16)	22 (18)
27	30 (13)	25 (19)	22 (22)	26 (14)
28	39 (7)	39 (13)	24 (26)	31 (14)
29	8 (22)	11 (23)	7 (21)	7 (23)
30	14 (24)	11 (27)	7 (28)	9 (27)
31	44 (9)	35 (17)	20 (24)	28 (14)

agreed (Whipple, 1949) that an average of about " 5·5 hours of clear sky per night is within a few per cent. of maximum clear sky available in North America."

Figure 2 is a map of Australia showing the average daily range of temperature. It should be easy to choose a place in any of the districts otherwise suitable for astronomical work that has a mean daily range of temperature less than 25 degrees, although it must be recognized that the need of a low temperature range is somewhat antagonistic to that of clear skies. However, the requirement of an elevated position does favour a low temperature range.

In regard to wind, little can be said unless specific localities are being examined. In general, the southern part of Australia is subject to westerly winds in the winter time and the northern parts have predominantly south-easterly winds, especially in the autumn and winter. The parts of New South Wales on the western side of the Blue Mountains have a high percentage of calm weather.

The altitude of any district which needs to be considered can, of course, be found approximately from atlases and larger scale maps, which are available from government departments responsible for survey work, and there is no need for the information to be given here.

I believe that the air over Australia is distinguished by high clarity. I have made a few measures of atmospheric extinction during the past year, although not as many as I had hoped, as the period I had set aside for it proved cloudy. A small camera and a guiding telescope were mounted equatorially on a portable stand, the guiding being done by hand without a driving clock. To photograph stars down to the fifth magnitude an exposure of 15 seconds was used. The plate was calibrated by photographing a number of stars near

the zenith with a wide range of magnitude and, when these stars were compared with another group photographed on the same plate at a low altitude, the effect of the atmosphere on the apparent brightness of the lower stars was obtainable. The star images were compared by medium of what has come to be called rather elegantly a " fly spanker ".

The results were analysed with the usual formula for atmospheric extinction

$$m_0 = m_1 - k(\sec\ z - 1)$$

where m_0 is the magnitude at the zenith, m_1 the apparent magnitude, z the zenith distance, and k is the coefficient of extinction determined to give values of m_0 consistent with the tabulated values for the various stars. The list of stars
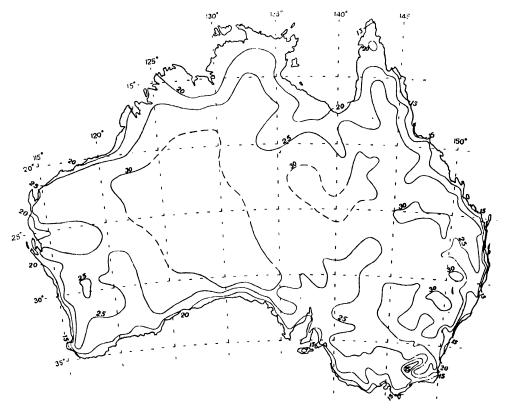
Fig. 2.—Mean diurnal temperature range (average maximum–average minimum) in degrees Fahrenheit. This map and Fig. 1 are published by courtesy of the Director of Meteorological Services.

selected for observation were all in spectral classes B and A, so that it could be hoped that errors in the estimated photographic magnitudes would not affect the result seriously ; and this does appear to be the case, especially when the extinction stars are very low and the effects of absorption larger than any error likely to occur. Even if the magnitudes used were not reliable and sec z not a sufficiently good approximation for the air mass in the formula, a *comparison* between sites would be obtained if the same methods and the same stars were used.

The following table gives the results which were obtained.

Place.	Long.		Lat.		Height.	Month.	No. of Nights.	k
	°	′	°	′	Ft.			
Orange	149	09	33	18	2,900	Dec., 1949	3	0·19
Sydney Obs. ..	151	12	—33	52	150	Dec., 1949	2	0·47
Toronto, N.S.W...	151	30	—33	0	50	Jan., 1950	1	0·40
Sugar Loaf Trig. Station	151	30	—32	54	1,300	Jan., 1950	1	0·28

No comment is necessary on these results except that the values are satisfactorily low, especially as they are in the ordinary photographic wave-lengths. A result similar to the one at Orange was obtained by Woolley and Gascoigne (1948) during their work on the magnitude of the Sun at Mt. Stromlo ;, this compares favourably with the values at the Lick and Mt. Wilson Observatories (Fath, 1935). The observations at Sydney were made when the sky appeared clear of industrial smoke as well as cloud.

As regards seeing conditions, it must be admitted that our knowledge is not sufficient, but astronomers and surveyors have given good reports of conditions in inland areas. H. C. Russell was enthusiastic about seeing conditions on the mountains west of Sydney, C. J. Merfield commented favourably on conditions at Wee Waa, New South Wales, and W. F. Gale on the seeing conditions at Armidale. Others who have worked in the country, and with whom I have had nights at the telescope in Sydney, have often remarked on the superiority of their atmosphere even on nights regarded as quite satisfactory.

Even such a brief review as this indicates that Australia has localities almost certain to be outstanding as astronomical stations. The districts of Canberra, Armidale, Warwick, Toowoomba and Alice Springs all promise well and if field tests were to be made it would be interesting to compare such an inland town of New South Wales as Dubbo with the others. Observations could also be made, where reasonable transport facilities exist, in regions 4, 5, 7, 9 and 21 of Figure 1 : Cue in Western Australia would be one. As far as freedom from cloud is concerned, these areas would be among the best in the world. Canberra has the advantage of having already a flourishing observatory and the Australian National University. These would be of much value to a research institution, as its staff would have the benefit of contact with others working in similar fields and of library facilities beyond those maintained within the institution itself. Of the meteorologically favourable sites, Mt. Stromlo is one of the farthest south, not only in Australia but in the southern hemisphere, with the south celestial pole highest. Armidale is on an extensive plateau with altitudes of more than four thousand feet available close at hand, and is the home of the New England University College. The claim of other places would rest chiefly on their meteorological advantages, or their ability to provide a high frequency of good seeing conditions.

EDUCATION IN ASTRONOMY.

One thing in which astronomy lags in Australia is in education. It is a strange deficiency, for the general public seem very interested and many hundreds visit Sydney Observatory each year. Astronomy is not mentioned in the calendar of several of our universities, and in most, only the astronomy used in connection with surveying is formally taught. At Sydney, it is one of the

choices available to students of mathematics after taking a first degree. Of course, a little astronomy necessarily appears in some other courses, such as physics and geography, and a number of Australian physicists have shown interest in astrophysical applications of their subject. In New South Wales, astronomy has recently been introduced into the secondary schools as a part of a general science course. In many universities in other countries, not only in America, England and Germany, but also in countries which have material resources of the same order as those of Australia, such as Holland or Argentina, astronomy may be taken as a full subject. It has played an exceedingly important part in the history of science, in the growth of scientific method, and in the development of the ideas we have of the universe and the place of world in it; as, for example, by the re-orientation of man's ideas at the time of Copernicus. Once again at the present time I believe a similar re-orientation, possibly attended by less bitterness, is taking place, as astronomy pioneers what may prove to be a knowledge of the structure of the universe as a whole. The discovery of gravity and of the finite velocity of light came from astronomy; and, although the only material which reaches our laboratories from outer space comes in the form of meteorites, one of the elements was first discovered on the Sun by an astronomer. We should not be content while there is no professor or lecturer in astronomy in an Australian university, as for example there is one in meteorology at Melbourne. Apart from the fact that astronomy deserves in its own right a place in tertiary education, some training at that level is necessary in order to equip teachers who will be undertaking teaching at secondary level.

In other countries the association between an observatory and a university has been found stimulating to both institutions, if indeed, an observatory run by a university can be regarded as a separate institution. Many of the observatories of the world are organized in such association, among them being the university observatories of London, Cambridge, Oxford and Glasgow in Great Britain, and nearly all of those of the United States of America. Most of these universities make available courses of study which leave the student with a thorough knowledge of astronomy and, if his inclinations and abilities are so directed, with technical equipment to engage in independent research. The University of Leiden, in Holland, is a famous one of these; and many Dutch astronomers occupy high positions in observatories all over the world. Another university which, to judge by its published plan of studies, gives a very complete and satisfying course in astronomy is the Argentine National University of La Plata, which also has a first rate observatory associated with it. Although I have been speaking of astronomy as a whole, I would like particularly to stress the need for teaching and research in fundamental astronomy, rather than in astrophysics, which appears to be able to look after itself very well. Now if a university department were being established in any subject it would be natural to consider whether its staff, by nature of the organization of the department and of the subject being studied, would have sufficient opportunity to do research work; and since fundamental astronomy has fallen somewhat into the background let me repeat that there are abundant opportunities in this field. Observations of good quality are needed for comparison with the ephemeris positions of various bodies for continual improvement of the astronomical constants; and, on the theoretical side, we must remember that the theories we have are based on observations of the motions of the planets only over a period of a few hundred years and the stability of the Solar System has so far only been studied with simplified assumptions, which may be justifiable in making a first approximation, but not in aiming for a definitive result. The researches of Poincaré form a wealth of material which has never been properly exploited. H. R. Morgan (1946) and G. M. Clemence (1947) in emphasizing

the importance of fundamental astronomy give many examples of recent or much-needed work in this field. Sir Edmund Whittaker (1949) in his article for the celebration of the centenary of the birth of Laplace last year, said :

" It is, in my opinion, to be regretted that at the present time, professional pure mathematicians . . . devote their attention to artificial examples constructed by themselves, instead of trying to solve the vastly more interesting problems of pure mathematics that are presented to us by nature. The remarkable properties of the expansions of Celestial Mechanics have never, so far as I know, been investigated by any of the pure mathematicians who specialize in questions regarding convergence of series."

To illustrate the activity that does exist, we may point to many recent researches in dynamical astronomy, as for example on the two body problem involving subjects such as apsidal motion of binary stars and the distribution of mass within them. Einstein and Infeld have only recently produced the theory of the double stars within the framework of relativity theory and the new knowledge being gained of the atmospheres of close binary stars shows that these give us a problem in dynamics which includes a close examination of the way in which stellar masses might vary and the effect that this would have on the evolution of the binary systems.

I do feel that, although Australia is doing work of which we may be proud, we should look forward to even wider grasping of the opportunities which undoubtedly exist. For this, one of the basic needs is a vital school of astronomy associated, if possible, with an observatory.

REFERENCES.

Brooks, C. E. P., 1930. *Mem. R. met. Soc.*, **1**, 127.

Buisson, H., Jausseran, G., and Rouard, P., 1930. *C.R. Acad. Sci.*, Paris, 190, 808.

Clemence, G. M., 1947. *J.R. astr. Soc. Can.*, **41**, 290.

Fath, E. A., 1935. *Lick Obs. Bull.*, **17**, 121.

Green, C., and Cook, J., 1771. *Philos. Trans.*, **61**, 397.

Maskelyne, N., 1786. *Philos. Trans.*, **76**, 426.

Meteorological Branch, Department of the Interior, Australia, 1945. **Maps of Average Monthly and Annual Rainfall, Australia.**

Middleton, W. E. K., 1941. Visibility in Meteorology. University of Toronto Press, Toronto.

Morgan, H. R., 1946. *Popular Astronomy*, **54**, 2.

Taylor, T. G., 1920. Australian Meteorology. Oxford University Press.

Whipple, F. L., 1949. *Sky and Telescope*, **8**, 90.

Whittaker, E. T., 1949. *Math. Gaz.*, **33**, 1.

Woolley, R. v. d. R., and Gascoigne, S. C. B., 1948. *Mon. Not. R. astr. Soc.*, **108**, 491.

DALTON–GUNNING AREA, N.S.W., EARTH TREMORS OF MARCH, 1949.

By G. F. JOKLIK, B.Sc.

With four text-figures.

I. INTRODUCTION.

On March 11th, 1949, severe earth tremors were felt in the Dalton area, and, less severely, over a considerable portion of New South Wales. These were succeeded in the epicentral area by numerous aftershocks during the following fortnight.

As officers of the Bureau of Mineral Resources, Geology and Geophysics, Canberra, G. M. Burton and the writer were detailed to investigate the tremors, and left Canberra on the first day of their occurrence. The greater part of the week devoted to the investigation was spent in the Dalton area. A reconnaissance embracing an area within a radius of some 40 miles of Dalton was also carried out with a view to determining the regional distribution of intensities, and the Chief Geologist circularized post masters and police officers stationed at fourteen N.S.W. towns from which some information about the tremors was to be expected.

On the party's return G. M. Burton was detailed to another field project and was thus unable to participate in the compilation of this paper.

II. GENERAL DESCRIPTION OF THE EARTH TREMORS.

The first shock, which appears to have been the heaviest in all areas affected, and which caused most of the reported damage, occurred at 8.31 a.m. (*a*), on Friday, 11th March. A strong aftershock was felt at 9.30 a.m. (*b*), and an even more noticeable one shook the epicentral area at 1.33 p.m. (*c*), causing further damage. The last severe aftershock took place at 11.24 p.m. on Wednesday, March 16th (*d*). These four principal shocks were the only ones noted by observers more than seven miles from the epicentral area, and shock (*b*) was felt only in a limited area in a southerly direction from the epicentre.

No preliminary phase preceding the main shock was reported anywhere. Shock (*a*) was very abrupt, and the most reliable estimates of its duration were approximately five seconds. Durations of the same order were assigned to the other principal shocks. The intensity of the main shock in the epicentral area was estimated as VIII on the modified Mercalli scale (see p. 25). The intensity gradient was very steep in all directions away from the epicentre.

The relatively dense population of the epicentral area facilitated the investigation. For almost ten days after the main shock this area was subjected to frequent slight aftershocks, none of them sufficient to cause further damage, although their abruptness caused considerable uneasiness amongst the local inhabitants. During the two or three days succeeding the main shock the aftershocks occurred at roughly half-hourly intervals, and less frequently during the latter part of this period.

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III. INSTRUMENTAL DATA.

Riverview Observatory, Riverview, N.S.W., and Brisbane Observatory both recorded the tremors. Unfortunately these are both situated on approximately the same azimuth from the epicentre. For the information given below in Table 1, the writer is indebted to Father D. O'Connell and Mr. P. F. Rheinberger, of the Riverview Observatory.

TABLE 1.
Data from Riverview Observatory.

Date.	E.S.T.			Distance from Riverview.	Azimuth from Riverview.
1949—	h.	m.	s.	Km.	
March 11 ..	8	31	36	190	240°
	13	33	54	190	240°
March 16 ..	23	25	24	190	240°

The distance and azimuth measurements correspond with an epicentre in the Dalton–Gunning district. The many small aftershocks mentioned in the preceding section were not recorded at Riverview. They appear to have been near-surface phenomena, most of them being accompanied by considerable sound effects.

On the morning of 13th March the party was favourably stationed in a two-story building under a corrugated iron roof at Yass for recording a series of tremors which were felt between 6.15 a.m. and 6.40 a.m. Details of the climax of this set of tremors, which occurred at 6.31 a.m., are recorded in Table 2.

TABLE 2.
Details of Tremors at 6.31 a.m., 13th March, 1949.

Duration of Tremor (secs.) ..	20		20		40		65		85*		60		60		25	20
Interval (secs.) ..		45		30		25		10		10		15		30	40	

The actual peak is marked with an asterisk, and at that stage a slight bumping of the floor was felt ; all the other shocks were gauged by the trembling of the corrugated iron roof. It is seen that, as the climax is approached, the shock period increases. Inversely, the interval between successive shocks decreases. Past the climax, the reverse holds.

IV. EFFECTS OF THE EARTH TREMORS.

(a) Damage to Property.

In all, some 150 persons were interviewed, and the properties of most of these were inspected. Press reports drew attention to damage in the township of Dalton itself, but it was found that landholders to the immediate east suffered more heavily.

Damage in the epicentral area included such items as heavily cracked walls, collapse of chimneys, collapse of timber stacks, shifting of heavy machinery,

collapse of poorly constructed walls, destruction of parapets, bursting of concrete water-tanks, breakage of pictures and property stacked on shelves, etc. The most spectacular damage was of course caused in the most poorly built structures. In the township of Dalton all the more modern buildings with the exception of one concrete edifice escaped serious damage. The Royal Hotel, which had previously been condemned, and the two churches, both very old buildings, received the greater publicity. In these three it was found, upon removal of

ISO - SEISMAL PLAN
DALTON - GUNNING AREA N.S.W.

Showing distribution, on modified Mercalli scale, of seismic intensities during earth tremors of March, 1949

SCALE OF MILES
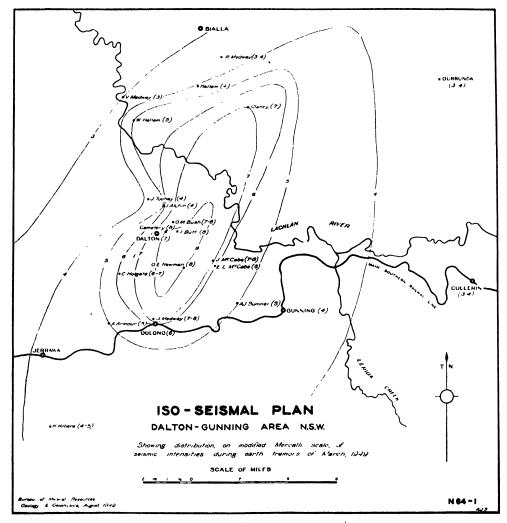
Fig. 1.

the plaster, that the walls were built of irregular granite and sandstone blocks the interstices between which had been filled with mortar, wood, and even paper. Numerous chimneys collapsed in the township, but here again it was found that the cement in most cases had crumbled.

The heaviest, though not the most spectacular, damage was inspected at the properties of O. E. Newman, J. Medway, I. Butt, J. McCabe and at the Dalton Cemetery (see Fig. 1). These define approximately the epicentral area.

DD

At the property of O. E. Newman, sawmiller, the earth tremors produced almost continuous rumblings for several days. A heap of sawdust was overthrown to the east, producing a complex pattern of fractures. Heavy wooden posts supporting the roofs of sheds moved relative to the earth, and the wheels of heavy machinery moved up to six inches in relation to the ground. In an outhouse the basement bricks were shifted by several inches. The brick fireplace was cracked, and all chimneys collapsed.

J. Medway's station homestead is a modern solidly-built brick house on good foundations. Cracks up to one-quarter inch in width, generally at a height of eight to nine feet above the ground, damaged the walls of every room, and large sheets of plaster were removed. Doorways built in a north-south direction were distorted; most objects had indeed been displaced to the north relative to the ground, suggesting that the shocks travelled north to south. Two concrete 2,000 gallon water tanks were fractured at the base, causing one of them to drain completely.

The house of J. McCabe was partly destroyed. It is situated on deeply weathered granite, and is built of loosely-cemented granite blocks. It is suggested that, had the building been of better construction, damage would have been slight.   .

Undoubtedly the heaviest damage to property was observed at the Dalton Cemetery. Two granite pyramids, four feet high, had been rotated through 20° in a clock-wise direction. Some slabs had been cracked, and in numerous graves the side-stones had moved away from the tombstone by three inches.

Outwards from the epicentral area damage was found to fall off rapidly. Outside a seven-mile radius from Dalton it was confined to an occasional fallen vase or bottle, and inhabitants mostly reported only the rattling of windows and crockery, and swaying of suspended lamps.

The results of the survey of the damage caused by the tremors suggest the following observations with regard to

(a) the suitability of different building materials in the Dalton area;

(b) the influence of the geological foundation on damage to buildings.

Faulty or poor construction is naturally associated with the greatest damage—it was this which led to the exaggerated press reports which followed the tremors. Solid and preferably deep foundations were found to be important. In houses of sound construction, the following materials are listed in their order of greatest resistance to shock, according to the present party's field observations :

(1) Fibro cement,

(2) Weatherboard,

(3) Brick,

(4) Concrete.

In the township of Dalton a concrete cottage which had not even been completed was damaged beyond repair. On the other hand C. Holgate's homestead, although within the epicentral region, showed very little damage; it is built of weatherboard on good foundations. Damage to effects within the house was severe.

The two main rock types in the Dalton area are massive granite and Palæozoic slate. Generally houses built on granite suffered more than those on slate. For example, the house of J. McCabe, built on granite, was partially destroyed, whereas that of E. L. McCabe, only 600 yards distant, on slate, suffered only slight damage. Two explanations could be given. The first is that the granite, with its deep zone of weathering, provides a less sound foundation than does the compact cleared slate. The second is that the granite, through its rigidity, transmits shock more abruptly than the slate, which, by virtue of its cleavage, is elastic and absorbs some of the shock.

(b) Surface Effects.

These included displacement of granite boulders, cracks in the ground, and slippage in alluvial banks.

On a granite hill only a few hundred yards east of O. Newman's house the following phenomena were observed : a granite block measuring $2' \times 3' \times 2'$ was displaced horizontally about three inches. Another block, $2' \times 1\frac{1}{2}' \times 1'$ moved down an inclined plane a distance of six inches. Half a mile south-west of O. Newman's house a block measuring $14' \times 8' \times 10'$ moved along an inclined joint plane, ploughing up the ground and damaging a tree. J. McCabe also reported movement of granite boulders near his house.

Only one crack in the ground was observed, namely on O. E. Newman's property. The trend of the crack was east-west, its length some 18 feet, width one-quarter inch, and the northern side had been displaced to the east a distance of about one-eighth inch. Many inhabitants reported earth cracks which opened during the principal shocks and closed immediately afterwards.

Several slippages of the banks were observed in the creek separating the properties of J. and E. L. McCabe. This dry watercourse is deeply entrenched in thick alluvium and detrital granite. Further minor slippages of this kind were noted in the creeks which spring from the western foot of Bald Hill, two miles east of Dalton.

V. GEOLOGY, PHYSIOGRAPHY AND THEIR RELATION TO THE POSITION OF THE EPI-CENTRAL AREA.

No geological map of the Dalton area was available, and a geological sketch map (Fig. 2) was accordingly compiled from field observations and aerial photographs.

Massive granite, which forms portion of the Gunning batholith, outcrops to the south and west of Dalton. Tertiary basalt flows cap all prominences to the north and west. The country rock is early Palæozoic slate containing beds of shale, sandstone and quartzite. David (1932) assigned an upper Silurian age to these rocks, but the maps published by the N.S.W. Mines Department indicate an Upper Ordovician age. The deposits are of deep-water marine origin and are, apparently, unfossiliferous.

Although the main portion of the granite is massive, definite granitized beds were observed at three localities. The most prominent one follows the chain of hills which trends in a northerly direction through the property of J. McCabe. To the north, roughly a mile to the east of Bald Hill, this granitized bed appears to be faulted out. It is found along the Gunning–Dalton road four miles to the south of Dalton. From the east and west of it, the Palæozoic slate grades into mica schist, strongly banded gneiss, and finally, into a thin band of massive granite.

A similar granitized bed is found along the Gunning–Bialla road, one mile north of the Crookwell turn-off. A remarkable feature of these granitized beds is that the kurrajong tree grows selectively on them. They bear little other vegetation. This peculiarity is apparently related to the original granitized horizons which appear to be offset in places, apparently by faults. This fact has significance in connection with the situation of the epicentral area.

The regional strike of cleavage and bedding is nearly north-south. In detail, variations from this direction are common. The pitch of subsidiary folds is generally to the north.

The western face of Bald Hill is traversed by a strongly mineralized shear-zone, in which the place of the slate is taken by slickenslided phyllite. There is no reason to believe that the shear-zone is connected with any present-day fault-action.

An excellent view is obtained from the summit of Bald Hill. Dalton is situated near the centre of a physiographic basin, some 15 miles in radius. Bald Hill is the highest eminence in a chain of hills which traverses the basin in a north-south direction. The range slopes steeply to the east and west and the faces could actually be termed scarps.

GEOLOGICAL SKETCH MAP
DALTON AREA, N.S.W.
Compiled from Aerial Photographs and from field observations
SCALE OF MILES
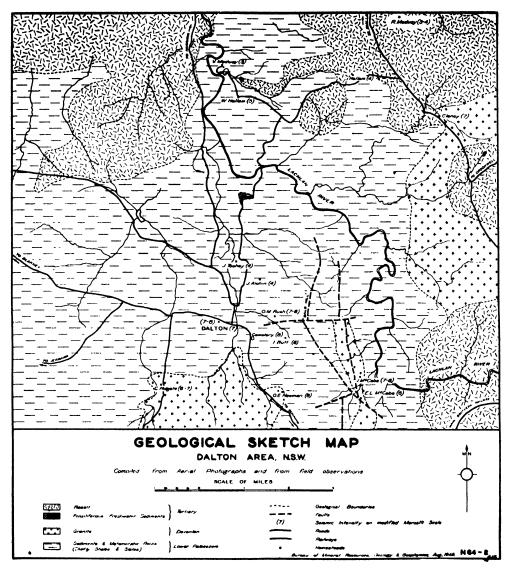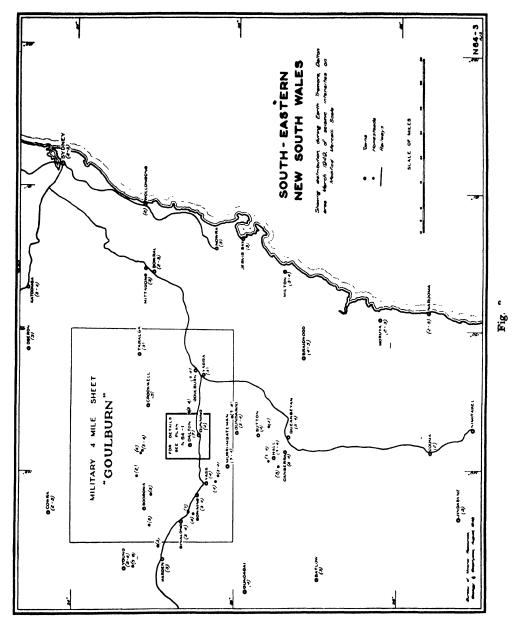
Fig. 2.

The theory is here advanced that the Bald Hill range forms an unstable block which is out of isostatic adjustment with its surroundings, and its efforts to reach isostatic equilibrium are the primary cause of the seismic disturbances in the Gunning–Dalton area.

Except where actual offsetting of the granitized bed was observed, the faults shown on Figure 2 are inserted on physiographic and air photograph

evidence only.   Close field examination would be necessary to confirm them.
There is little reason to doubt, however, that the " horst " is complexly faulted.

The fact that the chief evidence for some of the faults is physiographic
shows that movement must have taken place in recent times.   It is suggested

Fig. 6

that such movements are the means by which the " massif " is proceeding
towards isostatic equilibrium, and that the cause of the earth tremors is to be
found here.

There is one further point of evidence in favour of the theory that the
Bald Hill chain is a young upthrust block.   It has been stated that this eminence

stands alone in a physiographic basin of considerable radius. To the north and east of Dalton, however, some elevated terrain does exist, and, as is seen from Figure 2, Tertiary basalt forms cappings to it. The base of the basalt is found everywhere at the same altitude, and it seems that the lava was poured out over a peneplain.

Several of the hills in the Bald Hill chain have an altitude considerably in excess of the general basalt level, others are lower, yet nowhere is any sign of basalt found on them. The explanation could be that post-basalt uplift has caused removal by erosion of the lava sheet.

VI. Cause of the Tremors and Depth of Focus.

The cause of the tremors experienced in March in the Dalton–Gunning area appears to have been movement along faults in the Bald Hill block. Slight shocks have been felt at roughly six-monthly intervals as far back as the local inhabitants can remember. The process thus seems to be continuous, but at intervals of ten to twenty years relief is given to some residual stresses probably involving movement of greater magnitude.

A shallow focus is indicated by the distribution in time of the tremors and by the rapid falling-off in intensity away from the epicentre (see Figs. 1 and 2). In the case of a deep-seated or even intermediate focus, the Mercalli
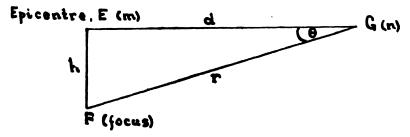
Fig. 4.

values VIII to V (see p. 25) would be expected to cover a far larger area if the seismic disturbance were severe or, if slight, the higher values would be absent and the gradient far less steep. Also the block-faulted Bald Hill chain is not a sufficiently large tectonic unit to have very deep-seated roots.

It has been mentioned that sound effects were prominent throughout the disturbance, which also indicates a near-surface origin for the shocks. Most of the inhabitants, in describing the tremors, spoke of " claps of thunder " and " reports of artillery ". The abruptness of the movements supports the same idea. Instead of strong trembling or swaying, the motion took the form of sudden jolts ; the former could be expected in a case of deep-focus disturbances, but the latter was the case even in all the innumerable after-shocks.

A rough determination of the focal depth was made by Oldham's method (Holmes, 1946, p. 364). The intensity is expressed in terms of numbers on the modified Mercalli scale (see p. 25). As these are not absolute quantities, an error is introduced.

In Figure 4

      m is the intensity at the epi-centre E,

      n is the intensity at any other point G,

      h is the depth of focus.

Then $\dfrac{n}{m} = \dfrac{h^2}{r^2} = \sin^2 \theta$.

In the present case, let E be a point midway between O. E. Newman's house and the Dalton cemetery, and let G be at Cullerin (see Fig. 2).

Then $\dfrac{n}{m} = \dfrac{7}{2 \times 8} = 0 \cdot 4375 = \sin^2 \theta$

$$\therefore \theta = 41° \ 25'.$$

Now (Fig. 1) $h = d \tan \theta$

and $d = 19 \cdot 8$ Km. $= 19 \cdot 8 \times 0 \cdot 8821$

$$= 17 \cdot 5 \text{ Km.}$$

From this the depth of focus would be of the order of fifteen to twenty kilometres, a value which agrees well with the description of the tremors so far given.

VII. THE ISOSEISMAL MAPS.

Throughout this report use is made of the modified Mercalli Scale of Earthquake Intensities. For convenience, a brief summary is included (Holmes, 1946, p. 363).

Intensity.

I	(<10)	Instrumental, detected only by seismographs.
II	(>10)	Very feeble, noticed only by sensitive persons.
III	(>25)	Slight, felt by people at rest.
IV	(>50)	Moderate, felt by people in motion.
V	(>100)	Rather strong, people are wakened, bells ring.
VI	(>250)	Strong, slight damage.
VII	(>500)	Very strong, cracking of walls, general alarm.
VIII	(>1,000)	Destructive, chimneys fall.
IX	(>2,500)	Ruinous, houses begin to fall.
X	(>5,000)	Disastrous, many buildings destroyed.
XI	(>7,500)	Very disastrous, few structures left standing, ground fissured.
XII	(>9,800)	Catastrophic, total destruction, objects thrown into air, ground badly twisted.

The numbers in brackets refer to the maximum acceleration of the ground in mm. per sec. per sec.

Figure 1 shows that the isoseismal contours take the form of ellipses where major axes trend in a north-north-westerly direction. They are, in other words, elongated approximately parallel to the Bald Hill chain which appears to be the " seat " of the tremors.

An anomaly is seen to the north-west of the epicentre, in which direction the intensity values fall off abnormally steeply. Figure 2 suggests no geological explanation. Two possible explanations are that :

(1) a portion of the block-fault system opposite the properties of J. Toohey and J. Alchin did not take part in the recent movements, or

(2) that the houses of these two landholders were unaffected by the tremors due to some favourable local geological conditions.

The regional map, Fig. 3, showing the distribution of seismic intensities over south-eastern N.S.W., has mainly statistical value. Information was partly obtained by correspondence. Inspection of the map shows that any attempt to contour on this regional scale would have failed, the low Mercalli values are distributed in too irregular a manner, and mostly correspond, in the writer's opinion, to local geological conditions or to different conditions of observation.

VIII. SEISMIC HISTORY.

The first earth tremor recorded from the Dalton–Gunning–Yass area occurred in 1885. Since then Riverview Observatory has recorded many pronounced and slight shocks, and local inhabitants have felt numerous minor tremors which were not strong enough to register at the Riverview.

The last tremors sufficient to cause damage shook the Gunning–Dalton area in 1934. The present party collected information concerning these, and an attempt is made to correlate them with those of March, 1949.

In Table 3 are listed, for comparison, the maximum amplitudes, recorded at Riverview, for the main tremors of 1934 and 1949.

TABLE 3.

Comparison of 1934 and 1949 Earth Tremors.

Date.	G.M.T.			Max. Amplitude (N.–S Movement) $(1\mu = 0.001$ mm.).
	h.	m.	s.	
1934—				
November 10	23	47	40	40μ
November 18	21	58	42	200μ
November 19	07	10	16	10μ
November 21	06	32	07	80μ
1949—				
March 10	22	31	36	170μ
March 11	05	33	54	34μ
March 16	15	25	24	7μ

The figures show that the phase of November, 1934, was more severe and sustained than that of March, 1949. When the local inhabitants were questioned regarding the relative severities, some gave the opinion that the 1934 tremors had greater force, others indicated those of 1949. The 1934 tremors were felt more severely at Gunning, and the Riverview Observatory gives the azimuth of these tremors as 235° and that of the recent ones as 240°, showing that the position of the epicentre for the 1934 tremors was to the south or south-east of that of the 1949 disturbance.

As an example may be quoted the houses of A. J. Sumner, two miles west of Gunning along the Gunning–Dalton road (see Fig. 1). In 1934 the building then in use was so severely damaged that it had to be abandoned. A new house, admittedly of a construction more suited to withstanding shock, was built only two hundred feet from the old one, and during the recent tremors only one chimney was damaged. No additional damage was suffered by the old house.

Enquiries indicated that during the 1934 tremors the zone of greatest damage ran through Sumner's property parallel to the recent epicentral zone.

It is suggested that the cause of both disturbances lay in the Bald Hill fault system. It has been proposed that this system acts in the manner of an active horst, and the theory is now advanced that, whereas in 1949 mainly the western side sought relief, it was the eastern flank which gave way to stress in 1934.

X. CONCLUSIONS AND RECOMMENDATIONS.

The obvious recommendations are that detailed geological mapping be carried out in the area to investigate more closely the possible cause of the

tremors, and that intending builders be made aware of the risk of using unsuitable materials for construction.

Regarding dam construction in the Australian Capital Territory and southern N.S.W., it is not thought that seismic disturbances in the Gunning–Dalton area so far experienced need have any influence on future plannings. The shallow focus and rapid falling-off of intensity indicate that outside a limited radius no damage to such structures is likely.

XI. REFERENCES.

David, Sir T. W. E., 1932. Explanatory Notes to accompany a New Geological Map of the Commonwealth of Australia.

Holmes, A., 1946. Principles of Physical Geology (Nelson), p. 364.

Milne, J., and Lee, A., 1939. Earthquakes and Other Earth Movements. (Kegan Paul.)

PALLADIUM COMPLEXES OF THIOETHERS.

Part I. The Reaction of Potassium Chloropalladite II with o-Methyl Mercapto Benzoic Acid.

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and J. Sorensen, A.S.T.C.,

Amongst the complex compounds formed in the platinum and palladium series those with ammonia and organic sulphides are usually analogous and comparable in properties. Chelating groups such as glycine are well known, and by using this compound cis and trans forms of diglycine palladium II have been prepared (Wardlaw, Sharratt and Pinkard, 1934).

In the sulphide series, compounds of platinum II with S-ethyl thioglycollic acid $(C_2H_5.S.CH_2.COOH)$ have been prepared (Beilstein) but to our knowledge no reaction of this type of chelating molecule with palladium II has been reported.

This investigation deals with the interaction of o-methyl mercapto benzoic acid (1), which functions as a bidentate group, and potassium chloropalladite. Interaction of 2 moles of (1) with 1 mole of K_2PdCl_4 yielded bis (o-methyl mercapto benzoato) palladium II, (2), sparingly soluble in cold water and organic solvents. This compound appeared stable in water and could be recrystallised from boiling water. In the presence of hydrochloric acid, however, the rings were readily opened and the dichloro compound (3), sparingly soluble in water and dilute acid, was formed. Recrystallisation of (3) from boiling water yielded the monochloro compound (4) formed from (3) by the expulsion of 1 mole of hydrochloric acid and the closure of one ring system. With 1 mole of sodium hydroxide in aqueous solution, closure of the second ring occurred, regenerating (2). Tentatively, trans structures have been assigned to these compounds.

Experimental.

(1) o-Methyl mercapto benzoic acid.

o-Mercapto benzoic acid, prepared as in Organic Syntheses, was methylated with $(CH_3)_2SO_4$ in alkaline solution. Recrystallised from alcohol-water. M.pt., 168·5–169° C. (Beilstein, 168–169° C.).

Found : S, 18·9%.

Calculated for $C_8H_8O_2S$: S, 19·06%.

(2) Bis (o-methyl mercapto benzoato) Palladium II.

K$_2$PdCl$_4$ (1·9 g. ≡ 0·006 mole) in 12 mls. of H$_2$O was added to the cold solution of (1) (1·95 g. ≡ 0·012 mole) in 20 ml. of H$_2$O and 8 mls. of 2N NaOH. Crude bis (o-methyl mercapto benzoato) palladium II precipitated and became crystalline on standing. Yield, 2·5 g. Recrystallised from boiling H$_2$O as canary yellow compound consisting of small needle-like crystals, with an acid reaction to litmus paper, and sparingly soluble in cold water and organic solvents. Dried over P$_2$O$_5$; M.pt. 192–194° C. (decomp.).

Found : Pd, 24·2% ; S, 14·4%.

Calculated for C$_{16}$H$_{14}$O$_4$S$_2$Pd : Pd, 24·19% ; S, 14·54%.

(3) Dichloro bis (o-methyl mercapto benzoic acid) Palladium II.

5·8 g. of (2) were dissolved in the minimum quantity of boiling water (850 ml.) and 50 ml. of conc. HCl added. The yellow solution became dark red and deposited a red-brown crystalline compound. On cooling, a further quantity of (3) crystallised (yield 5·45 g.) in well formed tetragonal prisms, amber in colour and giving an acid reaction on moist litmus paper. The substance decomposed but did not melt at about 240° C.

Found (on separate preparations, dried over P$_2$O$_5$) : Pd, 20·8%, 20·6% ; Cl, 14·0%, 13·7%.

Calculated for C$_{16}$H$_{16}$O$_4$S$_2$PdCl$_2$: Pd, 20·76 ; Cl, 13·80%.

(4) Monochloro (o-methyl mercapto benzoato) (o-methyl mercapto benzoic acid) Palladium II.

1·5 g. of (3) were dissolved in boiling H$_2$O (650 ml.). On cooling crystallisation did not occur and the solution was concentrated at the boiling point to 300 ml. On cooling (4) deposited as fine, bright orange prisms (yield, 1·1 g.), M.pt. 199° C. (decomp.), with an acid reaction on moist litmus paper.

Found : Pd, 22·4% ; Cl, 7·1%.

Calculated for C$_{16}$H$_{15}$O$_4$S$_2$PdCl : Pd, 22·34% ; Cl, 7·42%.

Regeneration of Bis (o-methyl mercapto benzoato) Palladium II.

0·55 g. of (4) were dissolved in 60–70 ml. boiling H$_2$O containing 11·5 ml. N/10 NaOH (≡ 1 mole of NaOH to 1 mole of (4)). After concentrating to 40 ml., (2) crystallised on cooling in bunches of thin, yellow needles. Yield, 0·35 g. M.pt., 194°.

Found : Pd, 24·1%.

Calculated for C$_{16}$H$_{14}$O$_4$S$_2$Pd : Pd, 24·19%.

SUMMARY.

The reaction of the sodium salt of o-methyl mercapto benzoic acid (≡SOH) with K$_2$PdCl$_4$ yields the palladium compound Pd(SO)$_2$, yellow crystals. In the presence of dilute HCl the Pd-O links are easily broken, forming the dichloro and monochloro compounds, (SOH)$_2$PdCl$_2$, amber crystals, and (SOH)(SO)PdCl, orange crystals, from which the original compound Pd(SO)$_2$ is regenerated by the action of NaOH.

REFERENCES.

Beilstein, 1928. Handbuch der Organischen Chemie. First Supplement, **3**, 95. Julius Springer, Berlin.

Blatt, A. H., 1943. Organic Syntheses, **2**, 580. John Wiley and Sons, London.

Pinkard, F. W., Sharrat, E., and Wardlaw, W., 1934. *J.C.S.*, 1012.

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NITROGEN IN OIL SHALE AND SHALE OIL.

XII. The Volumetric Determination of Basic Nitrogen in Shale Oils.

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INTRODUCTION.

One of the characteristics of shale oils is the presence of basic nitrogen compounds. If these are present in sufficient quantity they may be determined as the decrease in volume of the oil on washing with a dilute mineral acid. However, this method is sensitive to only $0 \cdot 05$–$0 \cdot 1$ per cent. of bases by volume (which is the same order as the tar base content of some of the samples), and, moreover, the result is adversely affected by the polymerization of the pyrroles present in the oil (Mapstone, 1948a) and by vapour losses from the volatile samples. In any case the volume of the tar bases is not a direct measure of the basic nitrogen content of the oil as the nitrogen content of the bases decreases with increasing boiling point. A search was therefore made for a more accurate yet simple method.

ACIDOMETRIC METHOD.

Various indicators were examined for their suitability for the acidometric determination of the weakly basic tar bases in aqueous solution. Purified samples of tar bases were analysed for total nitrogen by the modified Kjeldahl method (Mapstone, 1948b), and for basic nitrogen by dissolving various amounts in standard sulphuric acid and back titrating with standard sodium hydroxide solution using the different indicators. Screened methyl orange was thus shown to be the most suitable (Table 1), xylene cyanol FF as the screening agent giving sharper endpoints than methylene blue.

TABLE 1.

Comparison of Indicators for Acidometric Determination of Nitrogen Content of Tar Bases.

(Results as Percentage Nitrogen by Weight.)

Method.	Sample A.	Sample B.	Sample C.
Kjeldahl	$8 \cdot 20$	$8 \cdot 69$	$10 \cdot 62$
Back titration of acid solution using—			
Screened methyl orange ..	$8 \cdot 19$	$8 \cdot 74$	—
Bromthymol blue	$8 \cdot 11$	$8 \cdot 46$	—
Methyl orange	$7 \cdot 60$	$7 \cdot 88$	—
Screened methyl red ..	$6 \cdot 62$	$8 \cdot 36$	—
Methyl red	$6 \cdot 46$	$7 \cdot 80$	—
Phenolphthalein	—	—	$1 \cdot 09$

Several hydrocarbon samples were extracted several times with standard acid and then water washed, the extracts and washings being bulked and aliquots titrated. The results thus obtained were satisfactory but sometimes the extraction was incomplete or sharp separation of the oil and acid was difficult so further work was carried out to overcome these difficulties.

Two Indicator Titration.

A technique was sought to determine the weakly basic tar bases by the use of a two indicator titration analogous to that frequently employed for the determination of weak acid such as phosphoric and carbonic acids.

Preliminary experiments showed that screened methyl orange could be used as one indicator. Since the bases were slightly alkaline to phenolphthalein (Sample C, Table 1), and the orange colour of the acid extracts of all but the least discoloured samples interfered with the observation of that endpoint, the requirements of the second indicator were that its colour change be from colourless or yellow in acid solution to blue or green in alkali, and that its pH range be somewhat higher than that of phenolphthalein. Of those indicators which came close to these requirements thymolphthalein was found to be the most suitable.

Aliquots of a solution of a known weight of redistilled tar bases (from the gasoline) in dilute hydrochloric acid were rendered alkaline to thymolphthalein by the addition of an excess of barium hydroxide solution, followed by titration with standard hydrochloric acid, first to the thymolphthalein endpoint, and then to the screened methyl orange endpoint. (This procedure was adopted to prevent the colour of the screened methyl orange from interfering with the other indicator.)

The results, when expressed as the basic nitrogen content of the bases, were high but reproducible. This was found to be due to the need of a blank titration to allow for the wide pH range between the two endpoints $(3 \cdot 7 - 9 \cdot 5)$. This blank ranged from $0 \cdot 2$ to $0 \cdot 4$ ml. of $0 \cdot 1$N acid depending on the volume of the solution being titrated. When this allowance was made the basic nitrogen content $(10 \cdot 82\%)$ was in close agreement with the total nitrogen content $(10 \cdot 62\%)$ as determined by the modified Kjeldahl method.

The method worked satisfactorily for the determination of the bases from the gasoline but was not suitable for the higher molecular weight bases from the light recycle oil from the cracking plant, as the precipitation of the bases interfered with the observation of the endpoint. This interference, some features of which suggested that the precipitated bases may have extracted the indicator from the solution, was overcome by the addition of sufficient methyl or ethyl alcohol (generally about half the volume of the solution) to prevent the precipitation. This was further assisted by keeping to a minimum the total volume of the solution being titrated.

Extraction of Bases from Oil Samples.

In general it was found that two washes with hydrochloric acid were sufficient to extract all the bases from an oil sample provided that an excess of acid was present in each extract. With sulphuric acid it was necessary to have at least a 50 per cent. excess presumably because of the relatively weak second dissociation constant. The concentration of acid employed was relatively unimportant as long as there was an excess present at the last two, or preferably three washes. For samples containing less than $0 \cdot 1$ per cent. of basic nitrogen by weight 100–250 ml. samples could be conveniently extracted with $0 \cdot 1$N acid, but higher tar base concentrations were more conveniently extracted with approximately normal acid.

The technique found most suitable for an unknown sample was to extract a measured volume of the sample (100–250 ml.) with successive portions of 40, 20, 20, and 10 ml. of approximately 1N hydrochloric acid. (If the sample were known to have a low tar base content 0·1N acid could be used.) The extracts were bulked and made up to 100 ml. with distilled water; 10 ml. aliquots were rendered alkaline to thymolphthalein by the addition of a slight excess of barium hydroxide solution after the addition of 20–25 ml. of methyl or ethyl alcohol (necessary only with samples heavier than gasoline or with a very high tar base content). The solution was then titrated with 0·1N hydrochloric acid till the colour of the thymolphthalein was just discharged; four drops of the screened methyl orange were added and the titration continued to the second endpoint. If the second part of the titration required less than 5 ml. of acid it was repeated with a larger aliquot. A blank titration was then carried out using an equal volume of distilled water in place of the acid extract. The basic nitrogen content of the oil sample was then calculated as :

$$\frac{1 \cdot 4 \text{N} \ (\text{T–B}) \text{A}}{\text{V.D.E.}} = \text{per cent. by weight of basic nitrogen in sample}$$

where T = ml. acid required between indicators for aliquot,

       B = ml. acid required between indicators for blank,

       N = normality of acid,

       A = ml. of aliquot titrated,

       E = final volume of acid extract (normally 100 ml.),

       V = ml. of oil sample taken,

       D = density of oil sample.

TABLE 2.

Basic Nitrogen Content of Some Shale Oil Fractions.
(Results of Duplicate Analyses.)

Sample.	Basic Nitrogen. (Percentage by Weight.)
Crude shale naphtha	0·016, 0·017
Cracked shale gasoline—	
I	0·0399, 0·0401
II	0·0266, 0·0270
Topped gasoline—	
I	0·0633, 0·0637
II	0·0760, 0·0769
Recycle light oil—	
I	0·439, 0·431
II	0·655, 0·655
III	0·448, 0·451
Crude shale oil	0·146, 0·146

OXIDIZED OIL SAMPLES.

On standing oil samples tend to oxidize and discolour. Part of this colour was extracted by the acid and interfered with the observation of the thymolphthalein endpoint. Distillation of the oil samples before extraction was found to overcome this difficulty, the colouring materials being left in the distillation residue (0·5–1·0 ml.) which was shown to contain a negligible amount of bases. Discoloured samples were therefore redistilled before analysis.

CRUDE OIL SAMPLES.

Because of its wide boiling range crude shale oil could not be redistilled before analysis and the colour of the acid extract seriously interfered with observation of the thymolphthalein endpoint even when sufficient alcohol had been added to prevent precipitation of the bases, though it did not interfere significantly with the phenolphthalein endpoint. Further work showed that, with the crude oil bases, both these indicators gave the same endpoint, and that direct titration of the acid solution gave more consistent results. The crude shale oil tar bases were therefore determined in the acid extract by titrating alternate aliquots with standard carbonate-free alkali (e.g. barium hydroxide) to phenolphthalein and screened methyl orange endpoints, the tar bases being equivalent to the difference between the two sets of titrations.

Titration of the acid extract to the first permanent precipitate of tar bases required from 0·1 to 0·4 ml. more alkali than titration to the screened methyl orange endpoint and, by not diluting the acid extract before titrating the difference between the two methods of determining the excess acid could be taken as 0·2 ml. of 0·1N alkali when titrating 5–10 ml. aliquots. In this manner it is possible, if necessary, to make both the necessary titrations on the same aliquot.

SUMMARY.

A simple volumetric method has been derived for the determination of the basic nitrogen content of shale oil samples, based on a two-indicator titration of an acid extract.

REFERENCES.

Mapstone, G. E., 1948a. THIS JOURNAL, 82, 135-144.
————————— 1948b. Ibid., 82, 129-134.

NITROGEN IN OIL SHALE AND SHALE OIL.

XIII. An Approximate Method for Determining Pyridine Nitrogen in Oil Shale and Similar Materials.

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Introduction.

Various workers have observed that, for the determination of the nitrogen in pyridine type compounds by the Kjeldahl method, additional digestion time was required after the mixture cleared (e.g. Shirley and Becker, 1945 ; Cole and Parks, 1946). It was previously suggested by the author that this time factor might be able to be used as the basis of an approximately quantitative method for the determination of pyridine rings in an unknown material (Mapstone, 1948a). This paper presents the results of work carried out to test this hypothesis. Although they do not bear out their initial promise of an accurate quantitative method, it is felt that, as a qualitative and approximately quantitative method, they may be of interest.

Work Done.

The apparent nitrogen content of a number of nitrogen compounds of known structure was determined by the modified Kjeldahl method (Mapstone, 1948) for various times of after-boil (i.e. digestion beyond that required for the digestion mixture to clear). The results obtained (Table I) indicate that, in most cases, the oxidation was nearly complete after an after-boil of half an hour. At the end of one hour only those containing a pyridine nucleus or a reduced pyridine nucleus were incompletely oxidized. Of these, only pyridine itself was incompletely oxidized after two hours after-boil.

The proportion of the pyridine nitrogen evolved as ammonia after one hour's after-boil ranged from 60 per cent. for pyridine to 91 per cent. for acridine and isoquinoline. As a first approximation the proportion of the nitrogen evolved appeared to be a function of the amount of substitution in the molecule, but it was not possible to derive any quantitative relationships.

Somewhat similar results were obtained with the much milder digestion conditions obtained by not adding sodium sulphate to the sulphuric acid (Table I), to increase the temperature of the digestion, the pyridine ring compounds yielding from four to 42 per cent. of their nitrogen as ammonia with two hours' after-boil. Quinine (which contains both a pyridine and a quinuclidine nucleus) yielded 64 per cent. and piperidine gave 54 per cent. of its nitrogen in the same time. The other compounds examined which were not completely oxidized under these conditions were indole and its derivatives (80–92 per cent.) and some of the tertiary amines (69–100 per cent.).

Application of Results.

Since only pyridine type compounds were not completely oxidized with an after-boil of one hour in the presence of sodium sulphate, this method can be used for indicating the presence of pyridine rings in an unknown material.

TABLE I.
EFFECT OF AFTER-BOIL ON NITROGEN LIBERATED.
(Results quoted as Percentage of Total Nitrogen.)

Digestion time after clearing—hours	With 30 gm. Sodium Sulphate.						No Sodium Sulphate Added.								Error in Calculated Pyridine Nitrogen. Per Cent. Na$_2$SO$_4$.		Remarks on Digestion.
COMPOUNDS.	Nil	½	1	1½	2	2½	Nil	½	1	1½	2	2½	3	4	With.	Without.	
PYRIDINES—																	
Pyridine	48	3	60	86	96	100	45	32	34	29	32	—	—	—	−140	−9	No colour change after boil from cessation of frothing.
Shale Tar Bases	34	—	79	99	100	100	13	—	17	—	26	24	—	—	+21	−1	Normal.
Quinoline	13	24	75	100	100	—	1	—	4	—	18	—	—	—	−11	+9	Normal.
Isoquinoline	15	65	91	99	100	—	8	26	27	31	42	—	—	—	−52	−23	Normal.
Quinaldine	25	—	72	87	100	—	1	—	2	—	4	—	—	—	−50	+29	Normal.
Acridine	6	—	91	100	—	—	—	—	—	—	—	—	—	—	−55	n.d.	Normal.
8-Hydroxy Quinoline	55	45	88	89	100	—	4	9	16	23	27	—	—	—	−30	−3	No discoloration after boil from cessation of effervescence.
Quinine	86	65	81	98	100	—	49	55	57	—	64	—	—	—	+12	−52	
Piperidine	—	43	85	—	100	—	100	60	48	52	54	—	—	—	−8	−28	
PYRROLES—																	
Indole	94	98	100	—	100	—	71	85	87	—	92	—	—	—	Nil	+12	Normal.
2-Methyl Indole	92	97	100	100	—	—	65	65	71	82	80	—	—	—	Nil	+27	Normal.
Carbazole	90	100	100	—	—	—	68	100	100	100	88	78	—	—	Nil	+16	Normal.
Indigo Carmine	76	100	—	—	—	—	100	100	100	100	100	—	—	—	Nil	Nil	Normal.
Chlorophyll	99	100	—	100	—	—	n.d.	n.d.	n.d.	n.d.	n.d.	—	—	—	Nil	n.d.	Normal.
SECONDARY AMINES—																	
Di n-butylamine	87	97	100	—	100	—	87	88	85	92	97	100	—	—	Nil	+4	Normal.
Diphenylamine	91	96	100	100	—	—	86	80	84	93	—	—	—	—	Nil	Nil	Normal.
Thiodiphenylamine	79	97	—	100	—	—	79	93	—	96	100	—	—	—	Nil	Nil	Normal.
Indanthrene Blue	79	100	100	100	—	—	89	95	100	100	100	—	—	—	Nil	Nil	Normal.
TERTIARY AMINES—																	
Triphenylamine	57	78	100	100	100	—	44	50	57	64	73	—	—	—	Nil	+36	Normal.
Dimethyl Aniline	84	100	100	100	—	—	83	85	96	100	93	—	—	—	Nil	Nil	Normal.
Tri n-Butylamine	82	95	100	100	—	—	80	88	90	92	—	—	—	—	Nil	+9	Normal.
N , N' , Diphenyl-piperazine	93	100	100	100	100	—	60	61	65	67	69	—	—	—	Nil	+40	Normal.
MISCELLANEOUS—																	
Antipyrine	71	74	78	73	72	—	82	91	88	87	80	100	—	—	—	—	Gaseous nitrogen evolved during digestion. Remarks as piperidine.
Cyanuric Acid	100	100	100	—	—	—	91	89	100	—	100	—	—	—	Nil	Nil	
Melamine Formaldehyde Resin	79	100	100	—	—	—	58	80	90	100	100	—	—	—	Nil	Nil	Remarks as piperidine.
Uric Acid	80	95	100	—	—	—	64	80	96	100	100	—	—	—	Nil	Nil	Digestion time ×3.
Gelatine	99	100	100	100	—	—	89	95	98	100	—	—	—	—	Nil	Nil	Normal. Digestion time ×3.
SHALE AND PRODUCTS—																	
Shale	87	94	98	99	100	100	70	—	76	85	91	—	—	—	12	12	Normal.
Crude Shale Oil	76	87	94	100	100	100	—	—	—	—	67	—	78	80	36	44	Normal.
Petroleum Coke	89	98	99	100	100	—	71	—	—	75	77	—	—	—	6	31	Normal.

The three-fold range form nine to 28 per cent. of pyridine nitrogen not evolved from the samples (other than pyridine itself) means that it cannot be used for accurate quantitative work though roughly quantitative results could be obtained by assuming that one-sixth (16·66 per cent.) of the pyridine nitrogen remained undigested under these conditions. The error in determining in this manner the pyridine nitrogen content of the samples tested is also listed in Table I. This method (Method A) gave errors ranging from −52 to +21 per cent. with the exception of the case of pyridine itself.

In the absence of· added sodium sulphate, some materials other than pyridine compounds were incompletely oxidized by an after-boil of two hours. The error obtained by assuming that only one-quarter of the pyridine nitrogen was evolved under these conditions and neglecting other types of compound is also listed in Table I. This method (Method B) gave errors ranging from −52 to +40 per cent.

When applied to complex unknown samples, these approximate methods must be used with caution. The pyridine nitrogen content of crude shale oil, oil shale and petroleum coke, as determined by these two approximate methods, is given in Table II.

TABLE II.

Calculated Proportion of Pyridine Nitrogen in Various Samples.
(Results presented as percentage of total nitrogen content.)

Sample.	Total Nitrogen.	Proportion of Pyridine Nitrogen.		
		Method A.	Method B.	Known.
Oil shale	0·893%	12%	12%	Unknown.
Petroleum coke	1·630%	6%	31%	Unknown.
Crude shale oil	0·520%	36%	44%	Approx. 30%.

By both methods of calculation, the pyridine nitrogen content of the crude shale oil is slightly greater than the known basic nitrogen content of the oil (Mapstone, 1948*b*), but the small difference is well within the range of error observed with the pure pyridine compounds.

With the crude oil, and more particularly with the petroleum coke, Method B gave higher results than Method A. This may possibly indicate the presence of indole or stable tertiary amine structures in addition to the pyridine rings in these materials. The pyridine nitrogen content of the oil shale by either method was calculated to be 12·per cent. of the total nitrogen content. Since both methods give the same result the figure can be taken as of the correct order with a reasonable degree of confidence.

DISCUSSION.

This work confirms the relatively slow oxidation of the pyridine nucleus under the conditions of the analysis, as previously shown by the isolation of pyridine carboxylic acids from the Kjeldahl digestion products of coal (Beet and Belcher, 1938). The very slow attack of sulphuric acid on pyridine was shown by the fact that, even after two hours' after-boil in sulphuric acid without added sodium sulphate or one and a half hours in its presence, some pyridine was still distilled with the ammonia on rendering the mixture alkaline. This factor similarly affected the results with piperidine, most of which appeared to be initially oxidized to pyridine, and explains the relatively high results obtained

with both these materials after short digestion periods. Since the pyridine was first converted to a non-volatile and slowly oxidized compound, it is likely that the slowness of the oxidation is due to the difficulty of the further oxidation or sulphonation of pyridine sulphonic acid. The substitution of the pyridine nucleus as in its homologues and benz-derivatives appeared to facilitate the oxidation process as shown by the fourfold range of unoxidized material remaining after an hour's after-boil in the presence of sodium sulphate.

The reasons for the variations observed in the results appear to be mainly due to the effect of the molecular structure but it is probable that other factors, such as the rate of heating etc., are involved. For example, Crossley (1935) found that maximum nitrogen figures were obtained with the minimum heating rate to give the minimum " clearing " time, though no such relationship was observed in the author's previous work on the determination of the nitrogen content of oil shale and shale oil (Mapstone, 1948a). In the work reported in this paper, the heat input to the digestion was controlled to cause the sulphuric acid vapours to reflux in the bottom of the neck of the digestion flask, and was therefore approximately constant. It was noticed, however, that several-fold variations of the clearing time were sometimes obtained though the heating rate appeared to be constant.

Another factor in the application of the results is the absolute accuracy of the analytical method upon which the approximate methods of calculation are based. Duplicate analyses normally checked within one per cent. of the total nitrogen content for the complete digestion, but the accuracy was somewhat poorer when the digestion was incomplete. Assuming that the average accuracy of the analyses was two per cent. of the total, the possible error of the estimate of the pyridine nitrogen content of an unknown sample is twelve per cent. of the total nitrogen content. This possible source of error is somewhat reduced if the duplicate analyses check well with one another, a feature of the analysis of some materials but not of others.

SUMMARY.

Approximately five-sixths of the pyridine ring nitrogen in a sample are oxidized after an after-boil of one hour under standard conditions of the Kjeldahl method, the complete digestion requiring between one and a half and two hours. No other type of nitrogen compound examined interfered, so, in addition to being a qualitative method for detecting pyridine rings in an unknown substance, it can be used as the basis for a very approximate quantitative method. Similar results can be obtained by eliminating the sodium sulphate from the digestion mixture, but some other compounds interfere.

REFERENCES.

Beet, A. E., and Belcher, R., 1938. *Fuel*, **17**, 53.
———————————— 1938. *Mikrochemie*, **24**, 145.
Cole, J. C., and Parks, C. R., 1946. *Ind. Eng. Chem., Anal. Ed.*, **18**, 61-62.
Crossley, H. E., 1935. *J. Soc. Chem. Ind.*, **54**, 367-369T.
Mapstone, G. E., 1948a. THIS JOURNAL, **82**, 129-134.
——————— 1948b. *Ibid.*, **82**, 135-144.
Shirley, R. L., and Becker, W. W., 1945. *Ind. Eng. Chem. Anal. Ed.*, **17**, 437-438.

STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART II. SOME PROPERTIES OF TETRAMMINE PLATINUM II FLUORIDES.

By R. A. PLOWMAN, B.Sc., A.S.T.C. (Chem.).

In the previous communication (Plowman, 1949) the preparation of the fluorides and hydrogen fluorides of the tetrammine platinum II type was described. This communication reports the decomposition of these compounds on heating.

The results indicate that each tetrammine decomposes in a characteristic manner, which is related to the nature of the coordinating molecule attached to the platinum atom. The results can be represented thus : •

$$[Pt(NH_3)_4](HF_2)_2 \xrightarrow{140\text{-}150^\circ\ C.} [Pt(NH_3)_4]F_2 + 2HF \uparrow$$

$$[Pt\{C_2H_4(NH_2)_2\}_2](HF_2)_2 \xrightarrow{150^\circ} [Pt\{C_2H_4(NH_2)_2\}_2]^F_{HF_2} + HF \uparrow$$

$$[Pt(C_5H_5N)_4](HF_2)_2 \xrightarrow{170\text{-}200^\circ} \text{Simultaneous loss of HF and pyridine.}$$

In the ethylenediamine compound the remaining mole of hydrofluoric acid is held strongly, and on heating to higher temperatures no further evolution could be detected. The stability of this compound compares with the compound

$[Pt\{C_2H_4(NH_2)_2\}_2]^{F.H_2O}_{HF_2}$ obtained by crystallisation from aqueous hydrofluoric

acid and acetone (Plowman, *loc. cit.*).

The hydrated and anhydrous tetrammine platinum II fluorides decomposed completely at temperatures above 200° C. However, if the heating was conducted cautiously, the evolution of some ammonia could be detected at temperatures of 180–200° C. Tetrapyridine platinum II fluoride 3-hydrate commenced to lose pyridine above 100° C. and at 140° C. the loss corresponded closely with that of 2 moles of pyridine.

The above results are in reasonable accord with the known order of stability of the platinum-nitrogen bonds and with the structures which could reasonably be assigned to these compounds. Thus it is reasonable to expect hydrogen bonding to occur in $[Pt(NH_3)_4]F_2$ analogous to the type occurring in ammonium fluoride which crystallizes with the Wurtzite structure (Wells, 1945). In metal amines the difference in the electro-negativities between the nitrogen and hydrogen atoms permits of a considerable portion of the positive charge on the ion to be drained off to the hydrogen atoms (Pauling, 1948). Such a charge distribution would favour hydrogen bonding and contributions from structures such as

would be expected in $[Pt(NH_3)_4]F_2$. With the replacement of one hydrogen atom by an ethylene group such a symmetrical distribution would not be expected, leading to greater stability of hydrogen fluoride groups in the structure.

The decomposition of the fluoride and hydrogen fluoride of $[Pt(C_5H_5N)_4]^{++}$ indicate that stable compounds of the dipyridine series are formed. These are being investigated further and will be reported in a communication on the reaction of cis and trans $[(C_5H_5N)_2Pt(OH)_2]$ with hydrofluoric acid.

EXPERIMENTAL.

All reactions involving fluorides were carried out in platinum vessels.

The Action of Heat on $[Pt\{C_2H_4(NH_2)_2\}_2](HF)_2$.

At 103° C. evolution of hydrofluoric acid perceptible and at 150° C. hydrofluoric acid was issuing freely. A temperature of 165° was reached and the issue of hydrofluoric acid ceased after a few minutes. The crystals had lost their clear appearance and were white and powdery.

Found : Loss in weight, 4·2%.

Loss of 1 mole of hydrofluoric acid requires 5·1% ; 2 moles, 10·2%. In another experiment the compound was held at a temperature of 160–170° for 9 hours and then raised to 190° for a few minutes. Residue, pale yellow.

Found : Loss in weight, 6·6%.

In both cases residue increased in weight on standing almost regaining original weight. These reactions correspond most closely to

$$[Ptene_2](HF_2)_2 \xrightarrow[150°]{\Delta} [Ptene_2]{}^{F}_{HF_2} \xrightarrow{H_2O} [Ptene_2]{}^{F.H_2O}_{HF_2}$$

Between 190 and 200° C., decomposition was active, ethylene-ciamine is expelled and the residue became grey and black. The evolution continued up to 250°, when if the residue was now heated under a small flame decrepitation occurred.

The Action of Heat on $[Pt(NH_3)_4](HF_2)_2$.

At 150° C. for 1 hour, acid gas evolved and crystals lost clear appearance.

Found : Loss in weight, 10·0%.

At 140–150° C. and then temperature raised rapidly to 195° C. Residue started to blacken.

Found : Loss in weight, 10·1%.

Loss of 2 moles of hydrofluoric acid requires 11·7%.

Residue leached with water and crystallised by the addition of acetone.

Found : Pt, 58·9%.

Calculated for $Pt(NH_3)_4F_2.1·5H_2O$; Pt, 59·45%.

At 140–150° C. until all hydrofluoric acid is expelled and then raised slowly to 170–180°C. the evolution of some NH_3 was detected ; residue straw coloured.

Found : Loss in weight, 12·1%.

If the residue was now cautiously and quickly heated over a free flame, further evolution of NH_3 could be detected in the initial decomposition. Above 200° C., total decomposition started evolving dense white pungent fumes, with acid reaction ; black residue.

The Action of Heat on $[Pt(C_5H_5N)_4](HF_2)_2.0·5H_2O$.

At 100° C. the odour of pyridine was faint. At 130° C. a pale yellow colour was spreading throughout the mass. At 185–190° C. the substance melted to a dark brown liquid ; strong odour of pyridine followed by pungent acid fumes. Reaction appeared to cease after about 1 hour, when the substance solidified to a dark amber vitreous mass.

Found : Loss in weight, 25%.

Calculated : Loss for $2HF + 0 \cdot 5H_2O$, $8 \cdot 2\%$; loss for $2HF + 0 \cdot 5H_2O + 2C_5H_5N$, $34 \cdot 6\%$.

The residue was soluble in water, giving a dark amber solution. Preliminary investigations have indicated that the solution contains a compound in which $Pt : C_5H_5N : F = 1 : 2 : 2$. The compound is being investigated further and the results will be reported later.

The Action of Heat on $[Pt(C_5H_5N)_4]F_2.9H_2O.$

This substance readily loses $6H_2O$ over P_2O_5 (Plowman, *loc. cit.*). However, due to the rapidity with which the trihydrate takes up H_2O the 9-hydrate was used as a starting product.

(1) At 110° for 2 hours, odour of pyridine, and the residue was yellow and hygroscopic.

(2) At 140° for a further 2 hours, odour of pyridine and the residue was dark brown and hygroscopic.

Found : (1) Loss in weight, 24% (110° C.) ; (2) loss in weight, 36% (140° C.).

Calculated : Loss for $9H_2O$, $22 \cdot 8\%$; loss for $9H_2O$ and $2C_5H_5N$, 45% ; loss for $6H_2O$ and $2C_5H_5N$, $37 \cdot 4\%$.

SUMMARY.

The decomposition on heating of the fluorides and hydrogen fluorides of $[Pt(NH_3)_4]^{++}$, $[Pt(C_5H_5N)_4]^{++}$, and $[Pt\{C_2H_4(NH_2)_2\}_2]^{++}$ has been described. The hydrogen fluorides decompose in a characteristic manner depending on the nature of the coordinating addenda attached to the platinum atom. With $[Pt(NH_3)_4]F_2$ the temperature at which ammonia is lost and that at which total decomposition occurs are too close to effect a possible preparation of a diammine compound. However the compounds of $[Pt(C_5H_5)_4]^{++}$ show evidence of decomposing to compounds of the dipyridine series.

ACKNOWLEDGEMENT.

REFERENCES.

Pauling, 1948. *J.C.S.*, 1461.

Plowman, 1949. THIS JOURNAL, 83, 216.

Wells, 1945. Structural Inorganic Chemistry. Oxford, p. 259.

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STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART III. OXIDATION OF THE TETRAMMINE PLATINUM II FLUORIDES.

By R. A. PLOWMAN, B.Sc., A.S.T.C. (Chem.).

In a previous communication (Plowman, 1949) the preparation of the fluorides and hydrogen fluorides of the tetrammine platinum II type were described. This communication reports the preparation of some platinum IV compounds by oxidation of the corresponding platinum II types with hydrogen peroxide.

The compounds $[Pt(NH_3)_4]F_2$ and $[Pt\{C_2H_4(NH_2)_2\}_2]F_2$ were oxidised readily with hydrogen peroxide yielding the corresponding dihydroxo compounds, $[Pt_4(NH_3)_4(OH)_2]F_2.0\cdot5H_2O$ and $[Pt_4en_2(OH)_2]F_2.3H_2O$ as well defined, colourless, crystalline substances soluble in water. Salts of the $[Pt(NH_3)_4(OH)_2]^{++}$ ion have previously been described (Mellor, 1937), but as far as is known the fluoride has not previously been characterised. Compounds of the analogous ion $[Pten_2(OH)_2]^{++}$ do not appear to have been reported. Further investigation is being carried out on the reactions of this ion and the results will be reported in a separate communication.

When the above oxidations were carried out in the presence of concentrated hydrofluoric acid, the ethylene diamine compound yielded $[Pten_2(OH)F](HF_2)_2$ as a colourless crystalline compound, readily soluble in water. Oxidation of the $[Pt(NH_3)_4]^{++}$ ion in the presence of concentrated hydrofluoric acid yielded $[Pt(NH_3)_4(OH)_2](HF_2)_2$ crystallising in colourless prisms, soluble in water. The analytical results on this compound gave fluorine percentages that were slightly high (*ca.* 2–3%), whereas experience has shown that with a pure compound the fluorine percentage is usually low (*ca.* 2–3%). This may be indicative of the simultaneous formation of a compound analogous to that obtained with the ethylenediamine compound, viz. $[Pt(NH_3)_4(OH)F](HF_2)_2$. When an aqueous hydrofluoric acid solution of $[Pten_2(OH)F](HF_2)_2$ was evaporated to complete dryness at the temperature of the water bath the residue approximated in composition to $[Pten_2(OH)_2](HF_2)_2$. Solution of this residue in hydrofluoric acid (48%) and precipitation with acetone yielded a substance approximating to the original compound, indicating the existence of the equilibrium

$$[Pten_2(OH)F](HF_2)_2 + H_2O \rightleftharpoons [Pten_2(OH)_2](HF_2)_2 + HF$$

The oxidation of $[Pt(C_5H_5N)_4]F_2$ with H_2O_2 was not successful. The oxidation of the $[Pt(C_5H_5N)_4]^{++}$ ion with H_2O_2 was made the subject of a separate project, and preliminary investigations indicate that this ion is not oxidised with hydrogen peroxide. The results of these investigations will be reported in a later communication.

EXPERIMENTAL.

All reactions involving fluorides were carried out in platinum vessels.

(1) Dihydroxo bis (ethylenediamine) Platinum IV fluoride 0·5-Hydrate and 3-Hydrate.

$[Pt^{II}\{C_2H_4(NH_2)\}_2]_2F_2.2H_2O$ (Plowman, *loc. cit.*), 1·5 g., in 10–15 ml. of H_2O oxidised with 2 ml. of 30% H_2O_2. The solution was concentrated to 1 ml. on the water bath and on the addition of methanol-ether, (1) was precipitated as the 3-hydrate in agglomerates of small, colourless

crystals, very soluble in water, insoluble in acetone, alcohol and ether.   Yield, $1 \cdot 46$ g. $\approx 86\%$. Over P_2O_5 $2 \cdot 5$ moles of H_2O were lost, forming the $0 \cdot 5$ hydrate.   The $2 \cdot 5$ moles of H_2O were regained on exposure to air.

Found (compound dried over P_2O_5) : Pt, $49 \cdot 1\%$; F, $9 \cdot 3\%$; H_2O (increase in weight on exposure to air), $11 \cdot 3\%$.

Calculated for $[Pt^{IV}\{C_2H_4(NH_2)_2\}_2(OH)_2]F_2.0 \cdot 5H_2O$: Pt, $49 \cdot 2\%$; F, $9 \cdot 6\%$; increase for $2 \cdot 5$ H_2O, $11 \cdot 4\%$.

(2) Dihydroxo tetrammine Platinum IV fluoride, 0·5 Hydrate.

$[Pt^{II}(NH_3)_4]F_2.1 \cdot 5H_2O$ (Plowman, loc. cit.) $1 \cdot 5$ g. in 10–15 ml. H_2O oxidised with 2 ml. of 30% H_2O_2.   The solution was repeatedly evaporated on the water bath until excess H_2O_2 expelled. Crystallisation occurred on evaporation and was completed by the addition of acetone.   Yield, $1 \cdot 56$ g.—98% of (2) as clear colourless prisms soluble in water, insoluble in acetone, alcohol, and ether.   The compound commenced to decompose about 230° C. with simultaneous loss of NH_3 and HF.

Found : Pt, $57 \cdot 0\%$, $56 \cdot 8\%$; F, $10 \cdot 6\%$.

Calculated for $[Pt^{IV}(NH_3)_4(OH)_2]F_2.0 \cdot 5H_2O$: Pt, $56 \cdot 7\%$; F, $11 \cdot 0\%$.

(2) dissolved in cold H_2O yielded a sparingly soluble sulphate with sodium sulphate.

Found (material recrystallised from hot H_2O and dried over P_2O_5) : Pt, $49 \cdot 3\%$; S, $8 \cdot 3\%$.

Calculated for $[Pt(NH_3)_4(OH)_2]SO_4$: Pt, $49 \cdot 6\%$; S, $8 \cdot 14\%$.

(3) Dihydroxo tetrammine Platinum IV hydrogen fluoride.

$[Pt^{II}(NH_3)_4]F_2, 1 \cdot 5H_2O$ (Plowman, loc. cit.) dissolved in 2–3 ml. HF (48%) and the solution oxidised by the addition of 3–4 ml. 30% H_2O_2.   After evaporation $[Pt^{IV}(NH_3)_4(OH)_2](HF_2)_2$ crystallised in clusters of small jagged colourless prisms, with an acid reaction on litmus paper. Yield, $2 \cdot 06$ g.   Dried at 100° C. and finally over P_2O_5.   Deliquescent.

Found : Pt, $52 \cdot 4\%$; F, $21 \cdot 0\%$.

Dissolved in 3–4 mls. concentrated HF and recrystallised by the addition of acetone.

Found : Pt, $51 \cdot 7\%$; F, $20 \cdot 8\%$.

Calculated for $[Pt^{IV}(NH_3)_4(OH)_2](HF_2)_2$ Pt, $52 \cdot 0\%$; F, $20 \cdot 3\%$.

At 150° C. the compound lost HF, the loss being accompanied by some decomposition (slight blackening).

Found : 2 hours at 150–160° C., lost $14 \cdot 4\%$.

Calculated loss for 2 moles HF : $10 \cdot 7\%$.

(4) Fluoro hydroxo bis (ethylenediamine) Platinum IV hydrogen fluoride.

$[Pt^{II}\{C_2H_4(NH_2)_2\}_2]Cl_2, 2 \cdot 1$ g., in 10–15 ml. H_2O was treated with excess of freshly prepared Ag_2O.   To the filtrate excess HF was added and the solution evaporated to dryness on the water bath.   The residue, dissolved in 3–5 ml. of HF (48%), was oxidised with $1 \cdot 0$ ml. H_2O_2 (30%).   A few seconds after the addition of H_2O_2 a vigorous (almost violent) effervescence of gas occurred and the temperature of the solution rose markedly.   After evaporation on the water bath to incipient crystallisation, crystallisation of the soluble compound was completed by the addition of acetone.   Washed with acetone and finally with ether.   Yield, $1 \cdot 76$ g. of micro crystals colourless and slightly deliquescent after drying over P_2O_5.   The compound gave an acid reaction with moist litmus paper.

Found (compound dried over P_2O_5) : Pt, $45 \cdot 7\%$, $45 \cdot 0\%$; F, $21 \cdot 5\%$.

Calculated for $[Pt\{C_2H_4(NH_2)_2\}_2(OH)F](HF_2)_2$: Pt, $45 \cdot 5\%$; F, $22 \cdot 1\%$.

Dissolved in concentrated HF and recrystallised in two fractions by the addition of acetone.

Found (on first fraction) : F, $21 \cdot 9\%$; (on second fraction) : F, $21 \cdot 1\%$.

In a separate preparation, the solution after oxidation was evaporated to dryness on the water bath and finally dried in the oven at 100-105° C.

Found : Pt, 45·6% ; F, 18·6%.

Calculated for $[Pt\{C_2H_4(NH_2)_2\}_2(OH)_2](HF_2)_2$: Pt, 45·7% ; F, 17·8%.

Dissolved in 2-3 ml. HF (48%) and crystallised by the addition of acetone.

Found : Pt, 45·7% ; ·F, 20·3%.

At 120° C. the compound commenced to lose HF, and at 150-160° C. there was a steady evolution of HF.

Found : 2 hours at 150-160° C., 4·9% loss ; further 20 minutes at 165-180° C. (decomp.), 7·5% loss.

Calculated loss of 1 mole of HF : 4·7%.

The residue was deliquescent.

SUMMARY.

The preparation of some complex platinum IV fluorides and hydrogen fluorides has been described. These are $[Pten_2(OH)_2]F_20·5$ and $3H_2O$; $[Pt(NH_3)_4(OH)_2]F_2.0·5H_2O$; $[Pt(NH_3)_4(OH)_2](HF_2)_2$; and $[Pten_2(OH)F](HF_2)_2$. All were prepared from the corresponding platinum II compound by oxidation with H_2O_2. They are well defined, colourless crystalline compounds. The $[Pt(C_5H_5N)_4]^{++}$ ion was not oxidised with the same experimental conditions.

ACKNOWLEDGEMENT.

REFERENCES.

Mellor, 1937. Inorganic and Theoretical Chemistry, 16.
Plowman, R. A., 1949. THIS JOURNAL, 83, 216.

OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1949.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph, with the exception of number 195, which was an eye and ear observation. No correction was applied to the recorded times, either for personal effect or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the Nautical Almanac for 1938 and the reduction completed by the method given there. The necessary data were taken from the Nautical Almanac for 1949, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

Table I gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1949). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table II gives the results of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the Catalog of 3539 Zodiacal Stars for the Equinox 1950·0 (Robertson, 1940), as recorded in the Nautical Almanac.

TABLE I.

Serial No.	N.Z.C. No.	Mag.	Date.	U.T.	Observer.
				h m s	
187	647	5·5	Jan. 11	13 32 56·4	R
188	797	6·3	Jan. 12	12 29 44·7	R
189	771	6·1	Apr. 4	9 35 30·1	R
190	1365	6·1	Apr. 8	11 37 22·8	R
191	1684	7·0	May 8	11 31 29·4	W
192	1373	6·1	June 29	7 34 49·5	R
193	2063	6·7	Aug. 1	13 05 19·4	W
194	2317	6·6	Aug. 3	8 35 10·3	R
195	2468	6·9	Aug. 4	9 47 33·0	W
196	2644	6·3	Aug. 5	12 14 38·3	W
197	2270	5·4	Aug. 30	8 19 20·8	W
198	2583	5·8	Sept. 1	9 10 13·6	W
199	3197	6·5	Nov. 26	12 22 32·3	W
200	545	4·2	Dec. 4	9 39 46·8	W
201	552	3·0	Dec. 4	10 26 41·3	W

TABLE II.

Serial No.	Luna-tion.	p	q	p²	pq	q²	Δσ	pΔσ	qΔσ	Coefficient of	
										Δα	Δδ
							"	"	"		
187	322	+52	+85	27	+44	73	—1·3	—0·7	—1·1	+ 4·0	+0·95
188	322	+85	+53	72	+45	28	—2·4	—2·0	—1·3	+10·2	+0·64
189	325	+92	+39	85	+36	15	—1·4	—1·3	—0·5	+11·2	+0·52
190	325	+34	—94	12	—32	88	—2·8	—1·0	+2·6	+ 0·1	—1·00
191	326	+89	—45	80	—40	20	—1·0	—0·9	+0·4	+ 8·6	—0·82
192	328	+66	—75	44	—50	56	—0·8	—0·5	+0·6	+ 5·3	—0·92
193	329	+69	—73	47	—50	53	—0·4	—0·3	+0·3	+ 4·9	—0·94
194	329	+96	—28	92	—27	8	—0·6	—0·6	+0·2	+11·7	—0·52
195	329	+68	+73	47	+50	53	—2·5	—1·7	—1·8	+10·4	+0·63
196	329	+83	—56	69	—46	31	—0·4	—0·3	+0·2	+11·0	—0·56
197	330	+80	—60	64	—48	36	+0·4	+0·3	—0·2	+ 8·3	—0·80
198	330	+68	+73	47	+50	53	—1·2	—0·8	—0·9	+ 9·3	+0·71
199	333	+81	—58	66	—47	34	—0·6	—0·5	+0·3	+13·9	—0·22
200	333	+97	—23	95	—22	5	—1·7	—1·6	+0·4	+13·6	+0·06
201	333	+98	—22	95	—22	5	—2·0	—2·0	+0·4	+13·6	+0·07

REFERENCES.

Robertson, A. J., 1940.   Astronomical Papers of the American Ephemeris, Vol. X, Part II.
Robertson, W. H., 1949.   THIS JOURNAL, **83**, 64.
Sydney Observatory Papers, No. 9

THE GEOLOGY OF THE CANOWINDRA DISTRICT, N.S.W.

PART II. THE CANOWINDRA-COWRA-WOODSTOCK AREA.

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With Plate I and one text-figure.

CONTENTS.

I. INTRODUCTION.

The area considered lies immediately to the south of the district described in Part I of this series (Stevens, 1948).

Previous geological literature concerning the district is confined to brief notes (chiefly on mineral deposits) in some of the Annual Reports of the N.S.W. Department of Mines; a report on the limestones near Canomodine and Walli (Carne and Jones, 1919), and reports on dam sites on the Belubula River (Kenny, 1941; Mulholland, 1946). The latest regional map (1945) indicates the presence of Lower Palæozoic and Devonian strata, invaded by granite, but the area had not been previously mapped in detail.

The present paper is an attempt to explain the structure and stratigraphy of the region, and to correlate it with that of the Cargo district. Detailed accounts of the intrusive rocks will be reserved for later publications.

II. PHYSIOGRAPHY.

Two main streams drain the district—the Lachlan and Belubula Rivers. They follow meandering east-west courses in valleys about 1,000 feet above sea level, and join some distance to the west of the area considered. The divide between them runs roughly east-west, and is generally 500–700 feet higher.

The Belubula River has cut steep-sided, and sometimes vertical, gorges through the more resistant rocks (e.g. Silurian tuffs and cherts, and Devonian quartzites and conglomerates). In these places the physiography is relatively youthful; elsewhere the country is more mature, especially where the river flows through porphyry near Canowindra.

Outcrops are generally poor near the Lachlan-Belubula divide, but become better as the Belubula River is approached. The highest point in the area is Malongulli Trigonometrical Station (The Sugarloaf), 2,109 feet above sea level. It is not situated on the divide between the rivers, but owes its prominence to the superior resistance of its quartzite capping. The quartzites of the Conimbla Ranges and the granodiorite ridge between Cowra and Canowindra also form marked physiographic features.

III. PALÆOZOIC STRATA.

Ordovician.

Sedimentary rocks of Upper Ordovician age occur as narrow inliers between Malongulli Trig. Station and Woodstock. They are elongated north-south and are bounded on their western margin by a fault.

The rock types are mainly fine-grained sandstones and quartzites, some of which have a slaty cleavage. The following graptolites were collected by Mr. K. Sharp and the author (locality—one mile north of Woodstock, 810305*):

Diplograptus calcaratus var. *vulgatus.*
Diplograptus rugosus var. *apiculatus.*
Dicellograptus forchammeri var. *flexuosus.*
Dicellograptus angulatus.
Dicellograptus cf. *caduceus.*
Climacograptus bicornis.
Climacograptus tubiliferus.
Climacograptus cf. *minimus.*

Most of these rocks are in the zone of *Dicranograptus clingani* (the lower part of the Caradocian of Britain).

Silurian.

The Silurian rocks of the Cargo district extend south across the Belubula River towards Woodstock and Cowra. Slates, tuffs, cherts, limestones and occasional quartzites and conglomerates are the main rock types, and these are invaded by a garnet-bearing porphyry and the Cowra granodiorite. The andesites and tuffs east of Woodstock and Walli are also thought to be of Silurian age, equivalent to the Andesitic Series of Cargo. Thus, they would be the oldest of the Silurian system in the district.

The series consists of andesites of several types, interstratified with tuffs and breccias (as at Woodstock), slates and cherts. North-east of Woodstock, the andesites have large, closely-packed felspar phenocrysts. They are occasionally amygdaloidal as well, like those east of Canomodine Creek, Cargo. Quartz-epidote veins and traces of copper minerals are again characteristic of this series ; and in this district several barytes deposits (Raggatt, 1925) are associated with the andesites. Succeeding beds cannot be observed in this area because of faulting.

In the " Cranky Rock " area, fine-grained crystal tuffs overlie the Canomodine limestone. The tuffs are interbedded with, and grade into, cherts and slates. South-east of " Mountain View ", a high hill is composed of a conglomerate consisting of andesite pebbles. A similar rock has been noted on the east side of Liscombe Pools Creek (801472). Strata which include red to chocolate-coloured shales are adjacent to the garnetiferous porphyry south of " Cranky Rock ". They have been noted in many other localities, both in this district and to the north, at approximately the same stratigraphical horizon.

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* Six-figure numbers are grid co-ordinates on the one-inch military maps, Canowindra and Cowra. See also map (Plate I).

Next in the sequence is the garnetiferous porphyry, most of which appears to be a sill-like intrusive. It is generally conformable, though locally transgressive.

Slates, tuffs and some quartzites overlie the porphyry to the west. Some of the tuffs resemble the porphyry in hand-specimen, but the fragments are usually smaller and more closely packed than the phenocrysts of the porphyry. No large felspars occur in the tuffs, which appear to have a greater percentage of quartz in them.

East and south of " Mountain View " the strata are mainly slates (buff, greenish and red), with some tuffs and thin limestone beds. One limestone bed occurs at intervals along the west side of the porphyry belt of Liscombe Pools Creek, and another on the eastern side. Fossils found north-west of Woodstock (762350) and near " Malongulli " gate (788473) include *Tryplasma, Halysites, Favosites* and brachiopods. *Halysites, Favosites* and bryozoa occur in a limestone lens surrounded by porphyry and tuff on Liscombe Pools Creek (798470). These limestones and the associated strata are younger than the Canomodine limestone, and possibly younger than most of the tuffs which overlie it. (See text-figure.)

Correlation with the Cargo-Toogong District.

The first paper of this series (Stevens, 1948) expresses some doubt about the stratigraphical position of the Canomodine limestone. Although very similar to the parallel Cargo Creek belt, it seemed to occur at a higher horizon, separated from the Cargo Creek limestone by tuffs and slates. On following the Canomodine limestone south, it was found to be overlain by tuffs similar to those overlying the Cargo Creek limestone to the north. Comparison of the sequence on the Belubula River with that between the two limestones south of Cargo suggests that the Canomodine and Cargo Creek limestones are equivalent, and that the andesites and tuffs of Barrajin Trig. Station are equivalent to the Cargo Andesitic Series (see Table I).

TABLE I.

Comparison of the Silurian Sequences. (A) at the South-eastern End of the Canomodine Limestone, (B) in the Cargo Creek Area.

Sequence A.	Sequence B.
	Canomodine limestone.
	? Fault ?
4. Garnetiferous porphyry.	4. Garnetiferous porphyry.
3. Slates and cherts.	3. Slates and cherts.
2. Canomodine limestone.	2. Cargo Creek limestone.
1. Barrajin Trig. andesites and tuffs.	1. Cargo Andesitic Series.
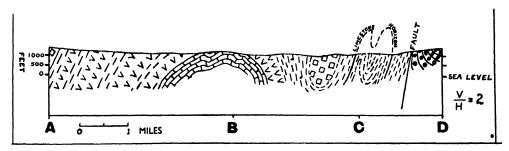
Upper Devonian.

Western Area. The Upper Devonian rocks of the Mandagery Range and Nangar Mountains (Stevens, 1948) continue south along the western boundary of the area mapped beyond the Cowra-Grenfell Road.

In the Mandagery Range, quartzites are the dominant rock type, but further south the proportion of interbedded shales and grits increases, giving rise to less rugged country, especially where the Lachlan and Belubula Rivers have cut through the series. As early as 1878, Wilkinson recognised Devonian rocks west of Canowindra, but the southern extension of this series is shown on all previous maps as Silurian. Wilkinson records *Lepidodendron, Sigillaria* and a " small bivalve shell " from these rocks.

Eastern Area. The Upper Devonian rocks of the Black Rock Range do not continue far south of the Belubula River, as they are cut off by a fault. An outlier of quartzite occurs east of the main belt, and on it Malongulli Trig. Station is situated.

The oldest beds are quartzites showing evidence of shallow water deposition in the form of ripple-marks and rain-prints. Etheridge (1909) records *Lepido-dendron, Lingula gregaria* and fish-plates from these rocks. Some thin beds of reddish shales occur within the quartzite series. Conglomerates follow, and these are overlain by red shales and green mudstones with plant remains.

IV. STRUCTURE.

Folding of the Palæozoic Strata.

Ordovician. Owing to the poor outcrops, the structure of the Ordovician rocks is uncertain, but from exposures one mile north of Woodstock it is probable that the folding is closer than in the Silurian and that an unconformity exists between them.

Silurian. Although the amplitude of the folds in the Silurian is much greater than in the Ordovician, the intensity of folding in the former series increases from west to east, as the major fault zone is approached. Angles of dip steepen, become vertical and the strata overturn on the margins of the porphyry upstream from " Cranky Rock ". Angles of dip are also very steep at the porphyry boundary on the Canowindra-Cargo Road ; in the headwaters of Binni Creek, and at the northern margin of the Cowra granodiorite.

The most striking major fold is the Cranky Rock plunging anticline, first noted by Kenny (1941) in an unpublished report on the Cranky Rock damsite. The structure in the Canomodine limestone is difficult to determine because of its massive nature, strong cleavage (N. 20° W.), and lack of fossil bands. It is possible that several minor folds exist within the limestone, as some have been observed south, and on the flanks, of the main outcrop. The most convincing proof of the fold is seen further south, where slates, tuffs and cherts dip gently under the porphyry, and the beds outcrop in a broad arc ; the fold plunging gently south.

The garnetiferous porphyry follows the strike of the beds except in the " nose " of the fold. The irregularity in outcrop here suggests a fault, but it may be due to a local transgression of the bedding planes.

South of the Cranky Rock anticline, another anticline emerges to the east of Tenandra Creek. It appears to plunge north, as the porphyry margin curves around, together with a change in strike. Minor synclines occur on the eastern flanks of both anticlines.

To the east, near Liscombe Pools Creek, all dips are either to the west or vertical, except for one near the major fault on the Belubula River. Over-folding is likely in this area, and both folds and faults suggest pressure from the west.

Upper Devonian.

Western Area. Except near the Conimbla Mountains, the Upper Devonian strata have not been followed far across their strike, but it is known that all the rocks dip west on their eastern margin. A synclinal structure has been noted west of Canowindra (Wilkinson, 1878).

The strike varies from N. 30° E. at Nyrang Creek to N. 30° W. north-west of Cowra. The dip varies from 18° to 90°. An anticline and south-plunging syncline are present between Conimbla Mountain and the Lachlan River ; this structure shows up well on aerial photographs, as the rock types are interbedded grits, quartzites and shales.

Eastern Area. The synclinal structure of the Upper Devonian in the Black Rock Range is cut off to the south by the southern continuation of the Columbine Mountain fault, and the narrow strip of Upper Devonian west of Malongulli Trig. Station dips steeply to the west. The outlier itself is in the form of a syncline with gentle dips ; almost a horizontal capping.

Faults.

The Southern Continuation of the Columbine Mountain Fault Zone.

North of the Belubula River the Columbine Mountain fault is joined by a fault from the north-west, and for several miles south the fault can be traced along the boundary of Silurian and Devonian rocks, the latter appearing to dip under the former. The Upper Devonian rocks are nearly vertical near the fault, and there is ample evidence of brecciation and shearing.

South of the point where the Upper Devonian rocks disappear Ordovician strata occur east of the main fault, and due to lack of outcrops the evidence of faulting is not as well defined. The main evidence for a fault along the western margin of the Ordovician north of Walli lies in the contiguity of strata high in the Silurian sequence and Ordovician rocks. However, some outcrops of iron and manganese ore (due to deposition along fault planes) occur along this boundary, as well as in the Ordovician strata.

Further south, the position of the fault is hidden by soil cover, but has been tentatively placed along the Ordovician-Silurian slate boundary. One mile north of Woodstock an outcrop of manganese ore occurs at the boundary of Ordovician sandy slate and Silurian sheared andesites. Faulting is clearly indicated.

Other Faults.

Two transcurrent faults have been noted east of Canowindra, where quartzite and slate beds have been displaced. A continuation of this line of faulting may be represented to the south-west by a zone of shearing in the porphyry and tuffs.

Minor faults displace a limestone lens and tuff beds near " Malongulli " gate, and signs of faulting occur between that locality and the head of Emu Creek.

The steep and sometimes vertical dip of the Upper Devonian quartzites along their eastern margin south-west of Canowindra suggests some faulting, and it is further exemplified by displacement of beds W.N.W. of Cowra.

Consideration of the stratigraphy of the area between Cargo and the Belubula River demands that, if the Cargo Creek and Canomodine limestones are equivalent, either a fault exists along the north-east margin of the Canomodine limestone or that an overfolded syncline occurs between the two beds.

V. INTRUSIVE ROCKS.

The Garnetiferous Porphyry.

The garnet-bearing porphyry previously seen near Toogong and Cargo continues south, and is well-developed near Canowindra. The rock is fairly uniform in appearance, except in shear zones. Idiomorphic phenocrysts of altered plagioclase and biotite, and corroded quartz, are present in a fine-grained groundmass.

The porphyry mass is mainly concordant, but tongues transgress the bedding planes of the associated sediments. It is noteworthy that the porphyry is restricted to the upper part of the Silurian, and has not been found invading the Andesitic Series or the Upper Devonian rocks. Where the porphyry outcrops strongly, large, rounded tors result; these are more pointed and elongated where the rock has suffered shearing.

Certain phases exhibit a clastic nature under the microscope; but this seems to be due to brecciation of an intrusive rock rather than evidence of a pyroclastic origin. In many places the porphyry is intrusive into tuffs of a similar mineralogical composition, and mapping of boundaries between the two rock types is difficult.

Similar porphyries and tuffs extend south through Boorowa to Yass, where three horizons of tuffs and similar intrusive porphyries have been recognised (Brown, 1940).

The Cowra Granodiorite.

This intrusion has a north-south elongation and is nearly conformable with the Silurian sediments, which dip towards it on the eastern side. It is intrusive into these sediments, which have suffered only slight metamorphism. On the western side, it is adjacent to the garnetiferous porphyry, but field relations are obscured by soil cover.

In hand specimen the rock is fairly uniform throughout the mass except for a narrow marginal phase (on the eastern side), which is a type of granite-porphyry. The usual type of Cowra granodiorite is a mottled black and white, phanerocrystalline rock with clear vitreous quartz, dull white felspars and idiomorphic lustrous biotite. · Red garnet is frequently present, often in or near the margins of xenoliths. The latter are abundant, especially near the southern end of the intrusion. Most of them have been completely recrystallised, but some retain the banding of the original sediment.

Nothing is known of the age of the intrusion beyond the fact that it is post-Silurian. It does not show any gneissic banding or marked orientation of minerals, so it is probably younger than Late Silurian and is possibly of Kanimblan age (Browne, 1929).

Minor Intrusions.

Most of the minor intrusions of the district occur near the major fault zone through Walli and Woodstock. The largest of these invades Ordovician strata south of Malongulli Trig. Station. The main rock type is a pyroxene lamprophyre, which weathers readily to a greenish-brown soil. This mass is intersected by dykes of a peculiar red rock consisting of perthite, green pyroxene, zeolites and quartz, with magnetite and apatite.

Further north, dykes of a finer-grained rock of similar mineralogical composition invade Silurian slates. It is considered that all these minor intrusions are related to one another, and to the granophyres and monzonite-porphyries of the Cargo district.

VI. Summary and Acknowledgements.

Ordovician, Silurian and Upper Devonian strata have been folded into plunging anticlines and synclines as in the Cargo district, of which the area considered is the southern extension.

The Columbine Mountain fault zone has been traced south towards Woodstock and an account is given of the faulted area between Walli and the Belubula River.

It has been shown that the garnetiferous porphyry, though locally intrusive, is mainly conformable with the Silurian sediments, and has been folded with them.

Introductory notes on the Cowra granodiorite are given, showing that it is an elongated, sill-like intrusion, almost conformable with the Silurian strata.

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Thanks are due to those members of staff of the Geology Department, Sydney University, who have given me assistance; also to Mrs. K. Sherrard, for determining the graptolites. The writer wishes to thank Mr. K. R. Sharp, Mr. G. Packham and other students for their help in the field; Mr. and Mrs. Whatmore of " Malongulli ", and Mr. and Mrs. W. Ridout of Walli for their hospitality.
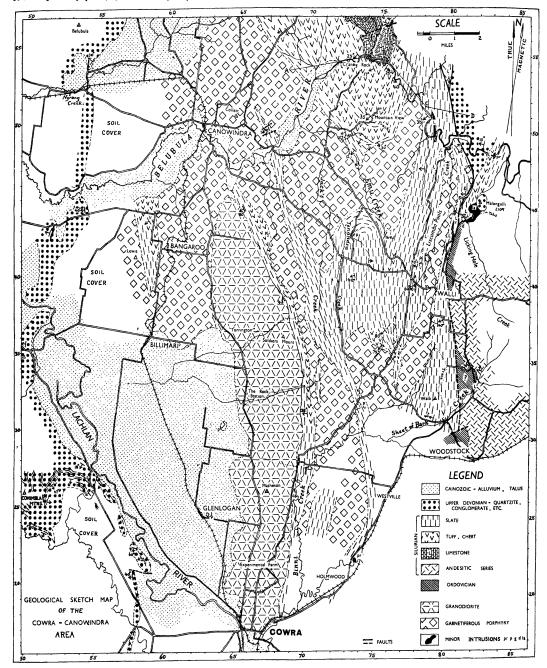
VII. References.

Brown, I. A., 1940. This Journal, 74, 312.
Browne, W. R., 1929. *Proc. Linn. Soc. N.S.W.*, 54, xxii.
Carne, J. E., and Jones, L. J., 1919. Geol. Surv. N.S.W., Min. Res. No. 25.
Etheridge, R., Junr., 1909. Geol. Surv. N.S.W., Rec. 8, pt. 4, 308.
Kenny, E. J., 1941. Unpublished report, Geol. Surv. N.S.W.
Mulholland, C. St. J., 1946. Unpublished report, Geol. Surv. N.S.W.
Raggatt, H. G., 1925. Geol. Surv. N.S.W., Bull. No. 16.
Stevens, N. C., 1948. This Journal, 82, 319.
Wilkinson, C. S., 1878. A.R. Dept. Mines, N.S.W., 150.

Explanation of Plate.

Plate I.

Geological sketch map of the Cowra-Canowindra area. Letters *pr, p, g, d, la* refer to minor intrusions related to porphyrite, garnetiferous porphyry, granophyre, dolerite and lamprophyre respectively.

GEOLOGICAL SKETCH MAP
OF THE
COWRA – CANOWINDRA
AREA

SCALE

LEGEND

CAINOZOIC – ALLUVIUM , TALUS

UPPER DEVONIAN – QUARTZITE ,
CONGLOMERATE , ETC.

SLATE

TUFF , CHERT

LIMESTONE

ANDESITIC SERIES

ORDOVICIAN

GRANODIORITE

GARNETIFEROUS PORPHYRY

MINOR INTRUSIONS pr p g d la

FAULTS

THE FIVE PROPERTIES CONCERNED IN THE TRANSPORT OF THE ACTIVE CORRODANT AGENT.

By R. C. L. BOSWORTH, Ph.D., D.Sc.

THE PROPERTIES INVOLVED IN DETERMINING THE RATE OF CORROSION.

An analysis of the process of the corrosive loss of matter in the simple case of a metal dissolving in a corrodant liquid without complications due to such phenomena as pitting, dezincification or of bimetallic corrosion, has been recorded in the three earlier papers of this series (Bosworth, 1949). The analysis revealed that for a given metal, in a given corrodant and at a given temperature, there are five properties concerned in determining the rate. These five properties, with the symbols suggested for them in parentheses, are :

(a) the maximum corrosion rate (q_0),

(b) the conductance term (j),

(c) the compliance term (K),

(d) the inertial term (ξ), and

(e) the electrochemical driving force (E).

The quantity q_0 is the rate at which the corrosion process will proceed, under the given conditions of temperature and pH, when the necessary depolarizing agent is made instantly available wherever required. The quantity j is a measure of the effective driving force change with ease of accessibility to the surface. K is a measure of the change of driving force with quantity of metal corroded by unit volume of the corrodant and ξ is a measure of that property which tends to maintain the reaction by maintaining the convective flow of corrodant to the surface under attack once the reaction is proceeding at a steady rate. ξ may be identified with an inertial (or inductive) term following the claim by the author (Bosworth, 1946) that natural thermal convection currents bestow an inductive character on the process of heat flow. ξ then is a property which indicates the magnitude of the opposition which the reaction offers to any change in rate.

The analysis in the earlier papers gave the product of the two properties K and E, viz. KE, but was not sufficiently complete to enable the two properties to be separated. More recently, however (Bosworth, 1949a), the magnitude of E for some of the systems studied has been obtained by polarization measurements so that for these systems it is possible to derive all five of the physical properties concerned in determining the rate of corrosion.

For example, for copper in 30% aqueous acetic acid at 20° C. we have, from overvoltage measurements,

$$E = 0 \cdot 70 \text{ volt.}$$

Previous measurements have given for this system

$$KE = 1 \cdot 20 \text{ mgrms. litres}^{-1},$$

G

so that
$$K = 1 \cdot 72 \text{ mgrms. litres}^{-1} \text{ volts}^{-1}.$$

Again, for copper in 60/40 acetic acid/acetic anhydride
$$E = 1 \cdot 10 \text{ volts}$$
$$KE = 2 \cdot 3 \text{ mgrms. litres}^{-1},$$
so that
$$K = 2 \cdot 09 \text{ mgrms. litres}^{-1} \text{ volts}^{-1}.$$

The other properties applying to these systems have all been recorded in the earlier papers (Bosworth, 1949), so that now a complete list can be given. Of these properties the value of K—the compliance term—and certain functions derived from K are of particular interest. Prominent among these derived properties are those having zero dimensions and those with the dimension of time.

THE MAGNITUDE OF THE COMPLIANCE TERM.

The property K is a measure of the change in concentration of dissolved metal required to produce a unit change in the corrosion cell e.m.f. E. Mathematically

$$K = \frac{\partial C_m}{\partial E} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots : . \quad (1)$$

where C_m is the concentration of the dissolved metal.

The variation of an electrode potential with the concentration C_c of the ion concerned in the electrode reaction is given by the Nernst equation :

$$E = E_0 + \frac{RT}{n F} \ln C_c$$

where R is the gas constant, F the faraday and n the valence of the ion.

At 20° C. this takes the value

$$E = E_0 + \frac{0 \cdot 0248}{n} \ln C_c$$

$$\text{or} \quad \frac{\partial C_c}{\partial E} = 40 \cdot 3 n C_c \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

Since the concentration of the dissolved metal C_m is connected by some stoichiometric relation with the concentration C_c of the ion concerned in determining the corrosion cell e.m.f., such as

$$dC_m = \lambda dC_c,$$

equation (1) may be transcribed to the form

$$K = 40 \cdot 3 \lambda n C_c \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

where λ is the ratio of the equivalent weight of the dissolving metal to the equivalent weight of the ion concerned in determining the corrosion cell e.m.f.

From the magnitude of K derived above we may thus obtain figures for the quantity $\lambda n C_c$. These figures are :

For copper in 50% aqueous acetic acid $= 0 \cdot 043$ milligrammes per litre.

For copper in 60/40 acetic acid/anhydride $= 0 \cdot 052$ milligrammes per litre.

Since λn is not expected to be greatly different from unity, we conclude that the concentration of the ion responsible for controlling the corrosion cell e.m.f. is of the order of $0 \cdot 05$ milligramme per litre. This particular fact may be used to eliminate certain mechanisms which might otherwise be postulated in explanation of the corrosion reaction. Thus the active depolarizing agent

cannot be copper ions in solution as the concentration of these ions is indeterminate in a fresh acid and much greater than 0.05 milligramme per litre in used acid. Again the concentration of hydrogen ions even in the non-aqueous solutions is many thousands of times greater than 0.05 milligramme per litre, so that the hydrogen ions cannot be effective corroding agent. This leaves dissolved oxygen as the only other obvious corroding agent. The concentration of dissolved oxygen in a saturated solution of acetic acid at $20°$ C. is about 0.2 milligramme per litre. It is not unreasonable to expect that the somewhat lesser figures of 0.05 might represent at least the order of the magnitude of the concentration of the dissolved oxygen in the vicinity of the surface undergoing corrosive attack.

From these considerations on the magnitude of the compliance term (K) we are thus lead to the conclusion that it is, most probably, the dissolved oxygen in solution which is responsible for the chemical rate controlling step in the corrosion process, and that, as this oxygen is used up by the corrosion process, the effective corrosion cell e.m.f. is progressively changed by a factor determined by the quantity K. The fact that the supply of an oxidizing agent is necessary for the maintenance of the corrosion of copper by organic acids has, of course, long been known on thermochemical grounds, and it is at least noteworthy that a purely physical analysis of the flow processes involved leads to the same conclusion.

DIMENSIONLESS QUANTITIES DERIVED FROM THE COMPLIANCE TERM.

In problems involving heat flow in fluid systems the dimensionless ratio known as the Prandtl number (Pr) has assumed great importance. Pr is the ratio of the diffusion constant for momentum, or kinematic viscosity (η/ρ) to the thermal diffusivity or thermometric conductivity ($k/C_p\rho$). The analogous properties in the transport process involving the conveyance of the active depolarizing agent is the ratio of the kinematic viscosity to the diffusivity of the depolarizing agent (D_c).

Let us use the symbol Pc for this dimensionless quantity—the analogue of the Prandtl number in corrosion problems. .

We have

$$\text{Pc} = \frac{\eta}{\rho D_c} = \frac{\eta K E}{\rho j} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (4)$$

All the properties concerned in equation (4) for the various systems studied have been measured and we have for

Copper in 30% aqueous acetic acid   ..   .. Pc$=1.90$
Copper in 60/40 acetic acid/anhydride   ..   .. Pc$=1.96$
Steel   ,,   ,,   ,,   ,,   ,.   .. Pc$=1.86$
Brass   ,,   ,,   ,,   ,, ... Pc$=2.16$
Phosphor bronze in 60/40 acetic acid/anhydride .. Pc$=2.08$

The relative constancy of the values of this property is perhaps significant and would appear to indicate that the transport of momentum and of the depolarizing agents in these corrodant liquids is effected by a similar molecular mechanism.

Another dimensionless quantity involving K is the expression

$$\frac{d^3 g \xi K^2 E^2}{\eta j (1 - q/q_0)}$$

which, as we have seen in the third paper of this series, plays a part in the corrosion reaction analogous to that played by the Grashof group in the natural convention of heat. Let us consider the possible variation of this

quantity with change in temperature. ξ, as we have seen, is the larger the lower the density of the original corrodant and thus is expected to increase slightly with increase in temperature. The quantity K, depending as it does on the solubility of a gas in a liquid, will decrease rapidly with temperature increase. E will, in general, change but slightly with temperature. The quantity j/KE, identified as a diffusion coefficient, and the viscosity will both change rapidly with temperature following an exponential-reciprocal relationship. Thus Barrer (1943) has written

$$\eta = \text{Const } e^{E_A/RT} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

$$D = \text{Const } e^{-E_A/RT} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (4)$$

Identifying j/KE with D_c, the diffusion coefficient for the active corroding agent we find that the quantity j/KE is independent of temperature unless the two activation energies of equations (3) and (4) are different. Accordingly we expect that the temperature variation of

$$\frac{d^3g\xi K^2 E^2}{j(1-q/q_0)}$$

will be largely dominated by the change in K and the quantity will thus assume lower values at higher temperatures. We have seen, however, that at low values of

$$\frac{d^3g\xi K^2 E^2}{\eta j(1-q/q_0)}$$

the quantity

$$\frac{qd}{j(1-q/q_0)}$$

will become practically a constant ; or, except for values of q approximating to q_0, the product qd is expected to be practically constant, or the rate of loss of matter from small cylindrical bodies by corrosion at high temperatures under quiescent conditions is expected to be proportional to the length rather than to the area. This particular phenomenon has already been noted in the third paper of this series in connection with the corrosion of copper cylinders at 70% C.

TRANSIENTS IN CORROSION PHENOMENA.

We have seen that the flow of matter in corrosion phenomena involves resistive, inductive and capacitative elements. Accordingly it is to be expected that the corrosion process will show transient phenomena. It is, of course, fairly common knowledge that the initial rate of corrosion may differ widely from that attained in the same system after the lapse of time (Speller, 1935). It now appears that we have, in some simple cases, a method of estimating the " time constant " for the corrosion process by analogy with what amounts to an equivalent electric circuit. In the systems which have so far been studied in this series the intensity of the convection current as estimated by the magnitude of the dimensionless quantity

$$\frac{d^3g\xi K^2 E^2}{\eta j(1-q/q_0)}$$

is relatively small and we may, as a first approximation, disregard the inductive element and estimate the time constant in terms of the resistance and the capacity.

Let us consider an area A under corrosion attack. Let V be the volume of the corrodant. The corrosion rate q is now given by

$$\frac{1}{q} = \frac{1}{q_0} + \frac{V}{Aj}$$

The corrosion cell e.m.f. (E) thus drives a mass current qA, or

$$\frac{q_0 j A^2}{jA + q_0 V}$$

so that the resistance term (R) is given by

$$R = \frac{(jA + q_0 V)E}{q_0 j A^2}, \quad \dots\dots\dots\dots\dots\dots\dots \quad (5)$$

The capacity term (C) is likewise given by

$$C = VK, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (6)$$

and the time constant (τ) by

$$\tau = RC = \frac{KEV^2}{jA^2}\left(1 + \frac{jA}{q_0 V}\right) \quad \dots\dots\dots\dots\dots\dots\dots \quad (7)$$

$$= \frac{V^2}{D_c A^2}\left(1 + \frac{jA}{q_0 V}\right) \quad \dots\dots\dots\dots\dots\dots\dots \quad (8)$$

The ratio $\dfrac{V}{A}$ is equal to the depth of the layer of corrodant over the surface,

while j/q_0 is the measure of the intercept of the $\dfrac{1}{q}$ versus z line on the axis, or a measure of the effective resistance of all factors concerned in determining the rate of corrosion other than those involving cathodic polarization, the measure being expressed in terms of the equivalent thickness (δ) of the quiescent layer of the corrodant. Equation (8) may thus be written

$$\tau = \frac{z^2}{D_c}\left(1 + \frac{\delta}{z}\right) \quad \dots\dots\dots\dots\dots\dots\dots \quad (8)$$

Expressions of a similar type for the resistance capacity time constants of transport processes hold for all diffusional systems (Bosworth, 1949*b*). Since values of D_c have been found for the various systems studied figures may be found for different geometrical configurations. For $1/D_c$ we may take 200 sec. cms. as a representative figure. For a metal covered to a depth of 1 cm. the time constant is therefore of the order

> 400 seconds or 6·3 minutes.

For a surface covered to a depth of 2 cms. this becomes

> 1200 seconds or 20 minutes.

and one covered by 10 cms.

> 22,000 seconds or 360 minutes.

The time constant, while varying roughly as the square of the depth of corrodant covering the surface under attack, is for any system of laboratory dimensions, small in comparison with a day and experimental determinations of the loss of weight over periods of five days or more should therefore not be subject to significant errors arising from the initial condition of unsteady state corrosion.

SUMMARY.

Corrosion of a metal by a corrodant liquid which attacks the surface uniformly is controlled by five physical properties: (*a*) the maximum rate, (*b*) a conductance term, (*c*) a compliance term, (*d*) an inertial term, and (*f*) the electrochemical driving force. All five factors may be determined by methods outlined in the previous papers.

In the case of copper in acetic acid the magnitude of the compliance term is shown to be dependent on the solubility of the corrodant for oxygen.

The rate of corrosion of a specimen freshly placed in a corrodant is expected to show transient phenomena, and where the contribution of the inertial element may be neglected the time constant for such transients is roughly proportional to the square on the depth of immersion of the specimen.

REFERENCES.

Barrer, R. M., 1943. *Trans. Farad. Soc.*, **39**, 48-59.
Bosworth, R. C. L., 1946. *Nature*, **158**, 309.
——————————— 1946. *Phil. Mag.*, **37**, 803-808.
——————————— 1949. The Influence of Natural Convection on the Process of Corrosion. THIS JOURNAL, **83**, 25.
——————————— 1949a. Anodic and Cathodic Polarization of Copper in Acetic Acid. THIS JOURNAL, **83**, 124
Speller, F. N., 1935. " Corrosion, Causes and Prevention ", pp. 10 *seq.*, 179 *seq.*, 212. McGraw Hill, New York.

THE MECHANISM OF THE FISCHER INDOLE SYNTHESIS.

By P. H. GORE,
G. K. HUGHES
and E. RITCHIE.

The mechanism suggested by Robinson and Robinson (1918, 1924) for the Fischer indole synthesis has been accepted as a satisfactory working hypothesis for many years. Consequently the theory of Pausacker and Schubert (1949*a*, 1949*b*) that the reaction proceeds by the free radical mechanism summarised below for the case of *cyclo*hexanone phenylhydrazone, required careful consideration.

Evidence along four lines was adduced in favour of this mechanism.

(*a*) It was found that a mixture of equal weights of *cyclo*hexanone *o*-tolyl-hydrazone and 2-methyl-*cyclo*hexanone phenylhydrazone on cyclisation by glacial acetic acid gave 11-methyl- and 8,11-dimethyl-tetrahydrocarbazolenines and after dehydrogenation of the neutral fraction, carbazole and 1-methyl-carbazole. These four products were formed in nearly equivalent proportions. (It may be remarked here that a fifth product, 1,8-dimethyl-carbazole, also would be expected in small amount according to both theories.)

From this result it was concluded that the Fischer indole synthesis is an intermolecular reaction and that homolytic fission of the N–N linkage occurs.

(b) From the cyclisation of *cyclo*hexanone 2-chloro-5-methyl-phenyl-hydrazone by dilute sulphuric acid, Pausacker and Robinson (1947) isolated not only the expected product, 8-chloro-5-methyl-tetrahydrocarbazole but also a small amount of a second substance to which the structure (I), with the name 12-hydroxy-7-methyl-1,2,3,4-tetrahydro*iso*carbazole given later (Barnes, Pausacker and Schubert, 1949) was assigned. Other substances of this type were subsequently obtained (Barnes, Pausacker and Schubert, *loc. cit.*).

(I)

It was claimed that the hydrolysis of the *o*-halogen in the substituted phenylhydrazone could be readily explained by the free radical mechanism.

(c) The well-known facile cyclisation of methyl *iso*propyl ketone phenyl-hydrazone may be explained, since the intermediate free radical (II) would be stabilised by hyperconjugation as in (III).

(d) The corresponding primary arylamines were produced in small amounts in the cyclisation of the phenylhydrazone, *o*-methoxyphenylhydrazone, *o*-tolyl-hydrazone and *o*-chloro-phenylhydrazone of *cyclo*hexanone (Barnes, Pausacker and Schubert, *loc. cit.* ; Pausacker and Schubert, *loc. cit.* (b)).

These facts were explained by the equation $Ar\dot{N}H + \dot{H} \rightarrow ArNH_2$.

However it can be shown clearly (1) that all of the evidence cited above can be satisfactorily interpreted without recourse to a free radical mechanism and (2) that there is convincing evidence that the cyclisation does not involve free radicals.

(a) These results may be very simply explained by hydrolysis of the hydrazones and recombination of the two hydrazines with the two ketones (or hydrazone interchange without the participation of water) to form four hydrazones, including *cyclo*hexanone phenylhydrazone and 2-methyl-*cyclo*-hexanone *o*-tolylhydrazone, not initially present, followed by intramolecular cyclisation. While the experiments described below were in progress this same explanation was suggested by Robinson and its possibility admitted by Pausacker (1949 ; Pausacker and Schubert, *loc. cit.*), who then found that the cyclisation of *cyclo*-hexanone *o*-tolylhydrazone in the presence of phenylhydrazine by glacial acetic acid gave a product from which carbazole could be isolated after dehydrogenation.

It has been known for many years that hydrazone interchange can occur (e.g. Freer, 1899 ; Frank and Phillips, 1949 ; for a beautiful example of the related case of semicarbazones, see Conant and Bartlett, 1932), and additional examples pertinent to the question of the mechanism of cyclisation have now been found. The experimental results may be summarised as follows :

(1) Acetone phenylhydrazone (1 mol.) and *cyclo*hexanone (1 mol.) boiled in glacial acetic acid for half an hour gave a 50% yield of tetrahydrocarbazole.

(2) Phenylhydrazine (1·2 mol.) and *cyclo*hexanone 2,4-dinitrophenyl-hydrazone (1 mol.) refluxed in glacial acetic acid for 24 hours gave an 18% yield of tetrahydrocarbazole and a 25% yield of 2,4-dinitrophenylhydrazine.

(3) *Cyclo*hexanone 2,4-dinitrophenylhydrazone (1 mol.) and acetone phenyl-hydrazone (5·3 mol.) refluxed in glacial acetic acid for 32 hours gave a 16% yield of tetrahydrocarbazole.

(4) Benzaldehyde phenylhydrazone (1 mol.) and *cyclo*hexanone (1 mol.) boiled in glacial acetic acid for 25 hours gave a 5% yield of tetrahydrocarbazole.

Now in the proposed free radical mechanism the radicals $C_6H_5\dot{N}H$ and $C_6H_{10}\dot{N}$ would be very reactive since they would not be stabilised by a large amount of resonance energy. Once formed, they would rapidly react further and it is unlikely that they would recombine to an appreciable extent. Hence according to this mechanism the critical step in determining whether a given hydrazone will cyclise is the formation of free radicals. Under the conditions used in the above experiments neither acetone phenylhydrazone nor *cyclo*-hexanone 2,4-dinitrophenylhydrazone cyclises. Therefore the formation of tetrahydrocarbazole in each of the experiments and the isolation of 2,4-dinitro-phenylhydrazine in experiment (2) must result from a hydrazone interchange and renders unnecessary the postulation of a free radical mechanism.

(*b*) This argument is valueless. The structures of the so-called tetrahydro-*iso*carbazoles are uncertain and even if they had the structures assigned to them it would still remain to be proved that they are formed from intermediates involved in the normal cyclisation. Moreover it is by no means apparent how the hydrolysis of the o-halogen in a substituted phenylhydrazone can be explained by the free radical mechanism.

(*c*) The ready formation of indolenines and carbazolenines is to be expected on the Robinsons' theory also. It is well known that carbonium ions with the formal positive charge on a tertiary carbon atom are formed more readily than those with the charge on a secondary carbon atom.

(*d*) If free arylimino radicals were formed then by analogy with the behaviour of other free radicals (Waters, 1946) they would be expected to react mainly with the solvent thus :

$$Ar\dot{N}H + HX \rightarrow ArNH_2 + \dot{X}$$

leading to the production of large, not small amounts of the primary arylamine. It is well known that phenylhydrazine can function both as an oxidising and reducing agent and it has also been found that by refluxing acetone phenyl-hydrazone with dilute sulphuric acid aniline is produced in small yield, even though cyclisation does not occur. Therefore the formation of primary aryl-amines is satisfactorily explained by oxidation-reduction. In support of this contention may be cited the fact that the cyclisation of *cyclo*hexanone 2,4,6-tribromophenylhydrazone gives comparatively high yields of 2,4,6-tribromo-aniline and 1,3,5-tribromobenzene (Barnes, Pausacker and Schubert, *loc. cit.*), Chattaway and Irving (1931) having shown that 2,4,6-trichlorophenylhydrazine is readily oxidised to 1,3,5-trichlorobenzene.

Three further arguments against the free radical mechanism can be put forward.

(e) Free radical reactions in solution are generally far from " clean " and usually do not give high yields (Waters, *loc. cit.*). By careful working a yield of over 95% of tetrahydrocarbazole can be obtained by the glacial acetic acid cyclisation of *cyclo*hexanone phenylhydrazone.

(f) Free phenylimino radicals would surely combine to give at least a trace of hydrazobenzene, which under the prevailing acid conditions would rearrange to benzidine. Tests which detect 0·00003 g. of benzidine gave negative results when applied to the appropriate fraction from the cyclisation of 39·5 g. of *cyclo*hexanone phenylhydrazone.

(g) Free radicals in glacial acetic acid solution would be expected to react extensively with the solvent mainly by the reaction

$$\dot{X} + CH_3COOH \rightarrow CH_3\dot{COO} + HX$$

which would be followed by

$$CH_3\dot{COO} \rightarrow \dot{C}H_3 + CO_2$$

and hence large amounts of carbon dioxide should be liberated. In a typical experiment the yield of carbon dioxide was only 0·4% mol./mol. of hydrazone. Moreover, it was found that when acetone phenylhydrazone was refluxed with acetic acid carbon dioxide was slowly evolved. This means that part of the carbon dioxide in the previous experiment was produced by a reaction not connected with cyclisation. The remainder may have arisen from some free radical reaction but in view of the very small amounts involved it is believed that its production is unrelated to the cyclisation. Tentatively it is suggested that it may be produced by thermal decomposition of the acetic acid, since much of it is evolved rapidly during the short strongly exothermic cyclisation reaction. It is thought that there may be present isolated points of high energy content resulting in the rupture of the acetic acid molecule before the energy can be otherwise dissipated.

<center>EXPERIMENTAL.</center>

<center>Products were identified by m.p. and mixed m.p. with authentic specimens.</center>

Formation of Tetrahydrocarbazole.

(1) A solution of acetone phenylhydrazone (4·1 g.; 1 mol.) and *cyclo*hexanone (2·7 g.; 1 mol.) in glacial acetic acid (25 ml.) was refluxed for half an hour and then cooled. Tetrahydrocarbazole (2·3 g.; 50%) m.p. 116-7° C. separated, and more was undoubtedly present in the mother liquor since it is moderately soluble in glacial acetic acid.

(2) A solution of *cyclo*hexanone 2,4-dinitrophenylhydrazone (5 g.; 1 mol.) and phenylhydrazine (2 g.; 1·2 mol.) in glacial acetic acid (35 ml.) was refluxed for 24 hours (not continuously). The dark solution was diluted with water and then shaken with an equal volume of ether, which took up the resinous material that had precipitated. After a few minutes orange crystals began to separate from the ether extract. The material (2·3 g.; m.p. 184-92° C.) which was collected after 18 hours was a mixture of *cyclo*hexanone 2,4-dinitrophenylhydrazone and 2,4-dinitrophenylhydrazine. The latter substance was obtained in pure form (0·9 g.; 25%) by three crystallisations from alcohol.

The ether mother liquor was washed with dilute acid and evaporated to dryness. The residue on steam distillation (600 ml. of distillate) afforded tetrahydrocarbazole (0·55 g.; 18%).

(3) Acetone phenylhydrazone (18·4 g.; 5·3 mol.) and *cyclo*hexanone 2,4-dinitrophenylhydrazone (6·5 g.; 1 mol.) in glacial acetic acid (45 ml.) were refluxed for 32 hours and then steam distilled. From the distillate 2,000 ml.), after acidifying with hydrochloric acid, tetrahydrocarbazole (0·65 g.; 16%) was obtained.

(4) A solution of benzaldehyde phenylhydrazone (2·4 g.; 1 mol.) and *cyclo*hexanone (1·2 g.; 1 mol.) in glacial acetic acid (45 ml.) was refluxed for 25 hours, and then steam-distilled. Tetrahydrocarbazole (0·1 g.; 5%) was collected from the distillate (800 ml.).

Action of Dilute Sulphuric Acid on Acetone Phenylhydrazone.

The conditions were those used by Barnes, Pausacker and Schubert (*loc. cit.*). Pure acetone phenylhydrazone (24·2 g.) free from aniline, was refluxed with water (65 ml.) and concentrated sulphuric acid (7·2 ml.) for half an hour. After cooling, the reaction mixture was extracted with ether, which on evaporation left unchanged acetone phenylhydrazone (4·0 g., 16%.) The aqueous layer was made strongly alkaline and extracted with ether, the extract dried and the ether removed. The residue was then fractionated under reduced pressure, the first few drops only being collected. From this distillate aniline (0·36 g.; 2·4%) was isolated through its hydrochloride and further identified through its 5-bromosalicylidene derivative. The residue in the flask contained phenylhydrazine (about 4·5 g.; 29%), determined by oxidation with Fehling's solution, which does not attack acetone phenylhydrazone.

Cyclisation of Cyclohexanone Phenylhydrazone.

Glacial acetic acid (190 ml.) was refluxed vigorously for 15 minutes in a stream of carbon dioxide-free nitrogen, then cooled and *cyclo*hexanone phenylhydrazone (39·5 g.) added. Traces of carbon dioxide were swept out, then the issuing gases passed through several gas wash-bottles containing barium hydroxide solution and the acetic acid solution carefully brought to its boiling point. At the moment of vigorous reaction carbon dioxide was evolved. When the reaction had subsided refluxing was continued for half an hour. The barium carbonate (0·17 g.; i.e. 0·4% mol. of·CO$_2$/mol. of hydrazone) was collected, washed and dried. The reaction mixture on cooling deposited tetrahydrocarbazole (26·8 g.) and a second crop (8·2 g.; total 98%) was obtained by evaporating the mother liquor to half bulk· and carefully adding water.

The second mother liquor was basified and shaken with an ethereal solution of the total tetrahydrocarbazole. The brownish yellow extract was washed with water and then shaken with dilute sulphuric acid (3 × 50 ml. of 3·2 N) when a slight amorphous brown precipitate (< 0·01 g.) formed at the interface. Neither this precipitate nor any of the acid extracts gave a positive test for benzidine with potassium dichromate or ferricyanide or carbon disulphide-bromine water.

Action of Glacial Acetic Acid on Acetone Phenylhydrazone.

When acetone phenylhydrazone (18 g.) was refluxed in glacial acetic acid (195 ml.) in a stream of pure nitrogen as above, barium carbonate (0·12 g.; 0·5%) was gradually precipitated during 2¼ hours.

REFERENCES.

Barnes, C. S., Pausacker, K. H., and Schubert, C. I., 1949. *J. chem. Soc.*, 1381.
Chattaway, F. D., and Irving, H., 1931. *Ibid.*, 1740.
Conant, J. B., and Bartlett, P. D., 1932. *J. Amer. chem. Soc.*, **54**, 2881.
Frank, R. L., and Phillips, R. R., 1949. *Ibid.*, **71**, 2804.
Freer, P., 1899. *Amer. chem. J.*, **21**, 14.
Pausacker, K. H., 1949. *Nature*, **163**, 602.
Pausacker, K. H., and Robinson, R., 1947. *J. chem. Soc.*, 1557.
Pausacker, K. H., and Schubert, C. I., 1949a. *Nature*, **163**, 289.
————————————————— 1949b. *J. chem. Soc.*, 1384.
Robinson, G. M., and Robinson, R., 1918. *Ibid.*, **113**, 639.
————————————————— 1924. *Ibid.*, **125**, 827.
Waters, W. A., 1946. The Chemistry of Free Radicals. Oxford University Press.

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THE PERMIAN ROCKS OF THE MANNING–MACLEAY PROVINCE, NEW SOUTH WALES.

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With Plate II.

INTRODUCTION.

In this paper is presented an account of the Permian rocks outcropping in the region embraced by the valleys of the Manning, Camden Haven, Hastings and Macleay rivers which will be called the Manning-Macleay Province. Details of a number of sections have been published in a series of papers dealing with smaller areas, but an attempt is now made to correlate the various beds throughout the whole province.

For reference purposes and in order to show the occurrences of the major units on a map it is suggested that the Macleay Series (Voisey, 1934), which probably corresponds to the Lower Marine Series of the Hunter Valley, may be divided into three stages as follows :

Warbro Stage, consisting of micaceous mudstones with small proportions of tuff, sandstone, shale, limestone and conglomerate, with a maximum measured thickness of 1,640 feet ;

Yessabah Stage, comprising calcareous sediments (including the Yessabah crinoidal limestone) and being very fossiliferous, with maximum thickness of 1,260 feet ; and

Tait's Creek Stage, consisting of chocolate and grey shales, sandstones and conglomerates with a maximum thickness of 500 feet.

This division, based on the lithology, is somewhat arbitrary and it is not suggested that a detailed correlation with Osborne's stages in the Hunter Valley should be made. There are, however, a number of similarities between some of the sediments and the faunas which indicate that the two sequences are of the same general age.

In a preliminary account of part of the province (Voisey, 1934) the name " Kempsey Series " was given to the sedimentary strata around Kempsey. Because of the paucity of outcrops subsequent evidence of age has only been obtained in one place, a quarry beside the Kempsey-Telegraph Point road, where marine Carboniferous shells were discovered. However, this information, together with Professor L. A. Cotton's discovery of *Rhacopteris* beside the same road, and lithological resemblances of some of the rocks to those in known sections, indicates that most, if not all, of the area shown as " Kempsey Series " on the map (Voisey, 1934, Plate XVI) should now be regarded as Carboniferous and not Permian as previously suggested. On the accompanying map (Plate II), therefore, a possible fault separating Carboniferous and Permian beds is shown running north-west from Kundabung.

MACLEAY SERIES.

Geographical Distribution.

The distribution of the three stages of the Macleay Series is shown on the map (Plate II). No occurrences are known north of the Kempsey Area Fault

and none south of the Manning River Fault System.   The chocolate or purple shales of the Tait's Creek Stage are revealed in road cuttings between Moparrabah and Yessabah but further south they are inconspicuous.   The crinoidal limestone of the Yessabah Stage may be picked up at intervals beyond Dondingalong as far as the old lime kilns near Kundabung.   Since outcrops become fewer to the south, the mapping of the continuation of the Permian beds is conjectural, being based on the topography and the soil.

The limestone and its associates reappear some miles to the south-west of Wauchope (Voisey, 1939b, 259).   Together with Carboniferous strata they are unconformably overlain by the Triassic sediments of the Lorne Basin, which form the Broken Bago Range.

Limestone is recorded from a place five miles west of the village of Comboyne, on the eastern side of a small tributary of Karagnine Creek, which flows into the Ellenborough River.   Carne and Jones (1919, 271) state that it is traceable for some distance down the gorge.   This belt continues southward to the neighbourhood of Wingham and Taree (Voisey, 1938 ; 1939c).

Numerous isolated Permian outcrops have been mapped in the Kimbriki-Mount George area, where they are separated from each other by the fractures of the Manning River Fault System (Voisey, 1939a ; 1939c).

Structural Relations.

The remains of the Permian deposits are preserved only in sunken areas within a large fault-girt block, which has been depressed relatively to its surroundings.

North of the Kempsey Area Fault Lower Palæozoic slates and phyllites appear, all Upper Palæozoic sediments having been removed by erosion. Similarly to the south, Devonian rocks are in contact with Permian and Carboniferous strata, demonstrating a smaller but still important movement.

Within this main down-thrown block the Macleay Series outcrops along the eastern limb of the Parrabel Anticline (Voisey, 1934) in synclines and small faulted blocks.

A critical examination of each locality where a section has been measured shows that only lower Permian rocks are present, and nowhere have the equivalents of the Coal Measures or Upper Marine Series been recognised.   The question as to whether a much thicker Permian sequence ever existed over the area must remain open.

The existence of the Triassic strata of the Lorne Basin (Voisey, 1939b) lying with a relatively gentle dip on the upturned edges of Permian and Carboniferous strata suggests that there was quite a long break between the onset of the Upper Palæozoic orogeny and the formation of the freshwater lake.   It may be, therefore, that the early orogenic movements which caused the folding of the older sediments took place a considerable time before the close of the Permian period.   As indicated in earlier papers (Voisey, 1939b, 254 ; 1939c, 406) the larger faults, the Kempsey Area fault and Manning River Fault system, occurred late in the orogeny and were responsible for the lowering of the block of already folded Upper Palæozoic sediments between them.   The Triassic lake formed in the depressed area perhaps a short time afterwards.

Stratigraphy.

Difficulties have been met in the field in the separation of the Kullatine Series and the Tait's Creek Stage of the Macleay Series since the Kullatine tillites in places weather to a chocolate or reddish colour not unlike that of the overlying shales (Voisey, 1936, 185).   The calcareous matrix of the shales containing glaciated pebbles at Yessabah and the marine fossils indicate that these beds are related closely to the Macleay Series.   In fact, the uppermost

shales are interbedded with the limestones of the Yessabah Stage and these also have a pink and sometimes purple colour. So close is the relation in this locality that the separation of the Tait's Creek and Yessabah Stages has to be quite arbitrary. This point is emphasised because W. R. Browne has now placed the Lochinvar shales in the Kuttung Series of the Carboniferous (Osborne, 1949, 207), and the Tait's Creek shales have been compared with these (Woolnough, 1911, 164).

Tait's Creek Stage. The Tait's Creek Stage is taken to include all beds above the Carboniferous Kullatine Series and below the Fenestellidæ Mudstone horizon (Voisey, 1934, 339).

There is a great variation in the nature of the sediments in this stage. Between Willi Willi and Yessabah they are largely chocolate and grey shales making up about 200 feet of the sequence, followed by 40 feet of green tuff. The shales contain a number of pebbles, some glaciated.

At Dondingalong sandstones form the basal unit but contain two lenticular bands of " shell conglomerate ".

In the Manning District tuffs and tuffaceous sandstones close to the base of the series also include a " shell conglomerate " of similar character containing marine fossils, including *Spirifer* and *Aviculopecten.* This rock appears in portions 117 and 118, parish of Taree, and portion 118, parish of Wingham near Western's Quarry. At Kimbriki and Mount George tuffs and banded mudstones are several hundred feet in thickness and directly overlie the Carboniferous tillites and tuffs.

Yessabah Stage. The division between this and the underlying Tait's Creek Stage is in each section placed where there is a definite increase in the amount of calcareous material. This seems to occur at approximately the same point throughout the province and represents some big change in the conditions of sedimentation. In contrast with the underlying Stage, the Yessabah Stage shows little lithological or faunal variation over an area representing probably 3,000 square miles of sea floor.
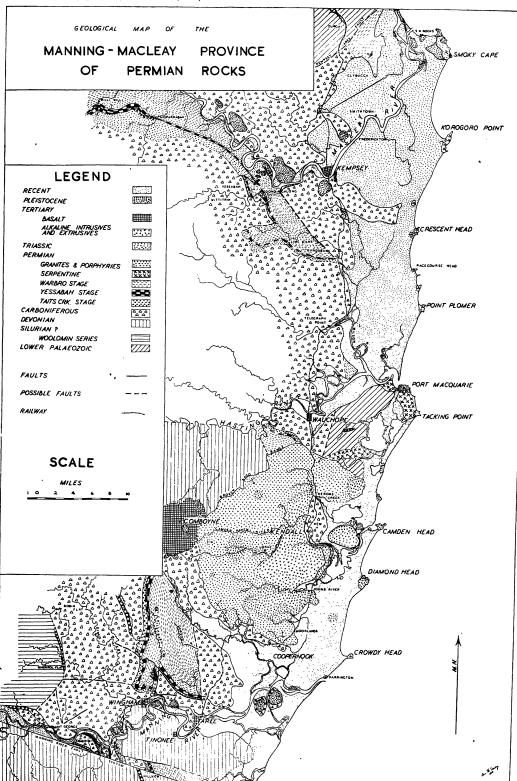
The Fenestellidæ Mudstones, which are generally well developed throughout the province, pass upwards and in some places laterally into limestones. The overlying Yessabah limestone has been used for the mapping of the whole province. Its upper and lower limits vary slightly from place to place, usually at the expense of the mudstones. The rock is coarsely crystalline and has been described as a marble. Fossils are well preserved in spite of the texture. The limestone varies somewhat in colour, usually being pink and purple in the north and grey to bluish-grey in the south. Towards Kimbriki it passes into a dark tuffaceous limestone losing much of its crystalline character.

The topmost unit of the Yessabah Stage is usually limestone, partly silicified, which weathers to a spongy mass of silicified fossil remains. Where *Cladochonus nicholsoni* is abundant, as at Willi Willi, macaroni-like masses occur.

Warbro Stage. A distinct change in lithology from limestones to micaceous mudstones and tuffs is recognisable in most localities. There is generally a sudden break in slope stratigraphically above the silicified limestone, the Warbro Stage sediments forming the lower ground.

Owing to the softness of the mudstones outcrops are infrequent, among the best being those in the cliffs beside the Manning River at Kimbriki (Voisey, 1939a). These show the richly fossiliferous *Linoproductus springsurensis* and *Strophalosia jukesi* beds to advantage.

The greatest variety of rock types in this stage is to be found in the parish of Warbro between Willi Willi and Moparrabah, where tuffs, conglomerates, mudstones and a band of limestone occur (Voisey, 1934, 339).

GEOLOGICAL   MAP   OF   THE

MANNING - MACLEAY   PROVINCE
OF   PERMIAN   ROCKS

LEGEND

RECENT
PLEISTOCENE
TERTIARY
    BASALT
    ALKALINE INTRUSIVES
    AND EXTRUSIVES
TRIASSIC
PERMIAN
    GRANITES & PORPHYRIES
    SERPENTINE
    WARBRO STAGE
    YESSABAH STAGE
    TAITS CRK. STAGE
CARBONIFEROUS
DEVONIAN
SILURIAN ?
    WOOLOMIN SERIES
LOWER PALAEOZOIC

FAULTS
POSSIBLE FAULTS
RAILWAY

SCALE

MILES

1 0 2 4 6 8 10

Geological map showing localities: TUNCA, S.W. ROCKS, SMOKY CAPE, CLYBUCCA, SMITHTOWN, FREDERICKTON, KOROGORO POINT, KEMPSEY, YESSABAH, WITTITRIN, DONDINGALONG, LIME KILNS, GUNDABONG, CRESCENT HEAD, RACECOURSE HEAD, POINT PLOMER, TELEGRAPH POINT, PORT MACQUARIE, WAUCHOPE, TACKING POINT, COMBOYNE, HERONS CREEK, KENDALL, KEW, SANDPIT FLAT, CAMDEN HEAD, DIAMOND HEAD, JOHNS RIVER, ROBIN, MOORLANDS, CROWDY HEAD, COOPERNOOK, BRINDLE FLAT, HARRINGTON, WINGHAM, ST GEORGE, TAREE, TINONEE, HILLVILLE, MANNING RIVER, MACLEAY RIVER, HASTINGS RIVER, M.N.

Palæontology.

The fauna of the beds consists essentially of fenestellids, crinoids and brachiopods, notably *Linoproductus springsurensis* and *Strophalosia jukesi*. Numbers of *Spirifer, Martiniopsis, Dielasma, Productus* and *Platyschisma* are present as in most other Permian sections. *Ptychomphalina* and a number of species of *Aviculopecten* occur in the Tait's Creek Stage at Yessabah, while *Eurydesma cordatum, Aviculopecten mitchelli, Tæniothærus subquadratus* and *Cladochonus nicholsoni* are prominent in the Yessabah Stage. The identification of the trilobite *Phillipsia* is noteworthy as it is not included in Osborne's lists from the Hunter River Valley.

Although *Linoproductus springsurensis* is well spread through the sequence it forms two well-marked horizons, one below the Yessabah Limestone in the Fenestellidæ Mudstones and one in the Warbro Stage above the limestone. The absence of this brachiopod and *Cladochonus nicholsoni* from the Hunter Valley sequences and their abundance in the Manning-Macleay Province and in Queensland suggest that there was a land barrier south of the Manning River. This is also supported by the change in the character of the Yessabah Limestone around Kimbriki and the fact that the Gloucester Coal Measures rest directly upon the Carboniferous lavas in the Gloucester Trough (Voisey, 1940).

As full lists of fossils have been given in earlier papers (Voisey, 1936, 1939a), they will not be repeated here.

SUMMARY.

The Macleay Series in the Manning-Macleay Province, which corresponds with part at least of the Permian Lower Marine Series of the Hunter River Valley, has been divided into three stages on lithological grounds.

The sediments occur only in synclines and faulted blocks. Higher members of the sequence, if any were developed, are no longer preserved. The fossils *Linoproductus springsurensis* and *Cladochonus nicholsoni*, which have not been found in the Hunter Valley sections but are present in Queensland, together with changes in lithology, indicate a land barrier between the Manning and Hunter rivers in Permian times.

ACKNOWLEDGEMENTS.

REFERENCES.

Carne, J. E., and Jones, L. J., 1919. Geol. Surv. N.S.W., Min. Res., **25**.
Osborne, G. D., 1949. *Proc. Linn. Soc. N.S.W.*, **74**, 203.
Voisey, A. H., 1934. *Ibid.*, **59**, 333.
——————— 1936. THIS JOURNAL, **70**, 183.
——————— 1938. *Proc. Linn. Soc. N.S.W.*, **63**, 453.
——————— 1939a. *Ibid.*, **64**, 241.
——————— 1939b. *Ibid.*, **64**, 255.
——————— 1939c. *Ibid.*, **64**, 394.
——————— 1940. *Ibid.*, **65**, 192.
Woolnough, W. G., 1911. THIS JOURNAL, **45**, 159.

37439

THE CHEMISTRY OF OSMIUM.

PART IV. THE PREPARATION AND RESOLUTION OF THE TRIS O,PHENANTHROLINE OSMIUM II ION.

By F. P. DWYER, D.Sc.,

N. A. GIBSON, M.Sc., A.R.I.C.,

and (MISS) E. C. GYARFAS, M.Sc.

Tris 2 : 2' dipyridyl osmium II bromide was prepared by Burstall, Dwyer and Gyarfas (1950) by heating a mixture of ammonium bromosmate IV with 2 : 2' dipyridyl at 280° C. The dark green complex ion Os(dipy)$^{++}$ was resolved through the antimonyl tartrate into stable optical enantiomorphs. The complex ion was reversibly oxidized at approximately 0·9 volt to the red Os(dipy)$_3$$^{+++}$ ion, which was also obtained in stable optical forms (Dwyer and Gyarfas, 1950).

The corresponding osmium II compounds with o,phenanthroline were ultimately prepared by heating the base with ammonium bromosmate in glycerol solution at 280–300° C. Mixtures of potassium hexachlor or hexabromosmate IV or potassium hexachlorosmate III with phenanthroline in aqueous alcohol could not be reduced to the compound with hypophosphorous acid in the same manner as the ruthenium compound (Dwyer, Humpoletz and Nyholm, 1946). Heating of a mixture of excess base and ammonium bromosmate in the absence of solvents, either with or without reducing agents such as ammonium hypophosphite, sucrose, lactose or formaldehyde, gave only very poor yields of the substance associated with osmium metal, and a large amount of tarry carbonaceous matter.

The compound was isolated from the glycerol mixture, after dilution with water, by addition of potassium iodide, and the sparingly soluble iodide was crystallized several times to remove traces of a very dark brown impurity. The very sparingly soluble perchlorate was obtained from the iodide by treatment with sodium perchlorate, and the soluble chloride by treatment with silver chloride. The salts crystallized in dark brown needles or flakes with a green reflex. They dissolved in water to form intensely dark greenish brown solutions, which were stable to strong acids and alkalis. In nitric acid the solutions gradually became red as a result of oxidation to the ion Os(phenan)$_3$$^{+++}$. The potential of the reversible reaction was approximately 0·9 volt. The oxidized solution, like the solutions of the ions Fe(phenan)$_3$$^{+++}$ and Ru(phenan)$_3$$^{+++}$, was not stable, and in the absence of excess oxidizing agent gradually became brown by the re-formation of the original osmium II complex ion.

The resolution of the tris o,phenanthroline osmium II ion was carried out in a similar manner to the ruthenium, iron and nickel complexes (Dwyer and Gyarfas, 1949), through the antimonyl tartrate. The dextro-form separated as the sparingly soluble antimonyl tartrate, which was transformed to the perchlorate. The lævo-perchlorate was obtained by addition of sodium perchlorate to the filtrate after the precipitation of the dextro-antimonyl tartrate. The complex ion was optically stable in boiling water, like the corresponding ruthenium compound. No rotation was observed in the Na$_D$ line, this wavelength being close to an absorption maximum.

The pure perchlorates gave $[\alpha]_{5461}^{25} = +3670°$ and $-3570°$. The corresponding ruthenium and nickel complex perchlorates gave $[\alpha]_{5461}^{25} = \pm 1330°$ and $\pm 1470°$ respectively.

The optical forms were oxidizable with ceric sulphate to optically active forms of the osmium III complex Os(phenan)$_3^{+++}$. It is hoped to be able to isolate the enantiomorphous forms of this complex ion in the solid form.

The redox potentials of this complex and the dipyridyl analogue will be discussed in a subsequent communication.

EXPERIMENTAL.

Tris o,Phenanthroline Osmium II Iodide Trihydrate.

Ammonium hexabromosmate (2·1 g., 1 mol.) in glycerol (40 ml.) was heated to 80–90° C. with stirring until the bromosmate had dissolved to a deep red solution. O,Phenanthroline monohydrate (3·6 g., 6 mols.) was added gradually at 120° C. and the mixture maintained at this temperature until the water was lost ; then the temperature was raised to 250–270 °C. whilst the mixture was stirred with a thermometer, and this temperature was maintained for 20 minutes. The dark brown mixture was cooled to below 100° C. and poured into 150 ml. of warm water. The mixture was acidified with hydrochloric acid (3–5 ml. of 5N.) and potassium iodide added. The dark greenish brown precipitate was washed with ether and ice water, and recrystallized several times from hot water and potassium iodide.

The substance crystallized in black flat flakes and prisms, was very soluble in methyl alcohol, but less soluble in ethyl alcohol and acetone.

Found : Os = 18·0% ; I = 24·6%.

Calculated for Os(C$_{12}$H$_8$N$_2$)$_3$I$_2$.3H$_2$O : Os = 18·3% ; I = 24·4%.

Tris o,Phenanthroline Osmium II Chloride Octahydrate.

The iodide (1 g.) in hot water (50 ml.) was shaken for 15 minutes with excess of freshly precipitated silver chloride. After filtering from silver halide the dark greenish brown filtrate was evaporated to 5 ml. on the water-bath and then to dryness over calcium chloride in a desiccator. The substance crystallized in very dark brown prisms with a greenish reflex.

Found : Os = 20·1% ; Cl = 7·47%.

Calculated for Os(C$_{12}$H$_8$N$_2$)$_3$Cl$_2$.8H$_2$O : Os = 20·1% ; Cl = 7·50%.

Tris o,Phenanthroline Osmium II Perchlorate Dihydrate.

The iodide (vide supra) (1 g.) in hot water (100 mls.) was treated drop by drop with sodium perchlorate solution (10%) with scratching the sides of the vessel. The sparingly soluble perchlorate crystallized as a brown microcrystalline powder. It was very soluble in methylalcohol

Found : Os = 19·5% ; N = 8·79%.

Calculated for Os(C$_{12}$H$_8$N$_2$)$_3$(ClO$_4$)$_2$.2H$_2$O : Os = 19·7% ; N = 8·70%.

d,Tris o,Phenanthroline Osmium II d,Antimonyl Tartrate Trihydrate.

The iodide (1 g.) in hot water (50 ml.) was transformed to the chloride as above and the solution cooled. Potassium antimonyl tartrate (1 g., 3 mols.) in water (20 ml.) was added gradually with scratching of the sides of the vessel. The antimonyl tartrate of the dextro-form was precipitated in fine brown needles. These were removed by filtration, washed with ice water and then dissolved in cold 0·05N sodium hydroxide solution and after filtration reprecipitated with acetic acid and a few drops of saturated potassium antimonyl tartrate solution. This purification was repeated three times. The substance was sparingly soluble in water to a greenish brown solution, but easily soluble in dilute acids and alkalis.

A 0·006% solution in 0·01 NaOH gave $\alpha = +0·10°$ (1 dm. tube), whence $[\alpha]_{5461}^{25} = +1700°$.

Found : Os = 13·9% ; N = 6·18%.

Calculated for Os(C$_{12}$H$_8$N$_2$)$_3$(C$_4$H$_4$O$_6$.SbO)$_2$.3H$_2$O : Os = 14·0% ; N = 6·20%.

H

d, Tris o,Phenanthroline Osmium II Perchlorate Monohydrate.

The antimonyl tartrate above was dissolved in cold $0.05N$ sodium hydroxide and precipitated with sodium perchlorate solution (10%). The resulting precipitate was crystallized several times from hot water by the addition of sodium perchlorate. The substance crystallized in small dark brown rods with a green reflex. It was more soluble than the *d,l* perchlorate.

A 0.003% solution in water gave $\alpha = +0.11°$ (1 dm. tube), whence $[\alpha]_{5461}^{25} = +3670°$ and $[M]_{5461}^{25} = +34,800°$.

In the sodium D line no rotation could be observed.

The solution was optically stable at room temperature and at 100° C.

Found : $Os = 20.1\%$; $N = 8.93\%$.

Calculated for $Os(C_{12}H_8N_2)_3(ClO_4)_2.1H_2O$: $Os = 20.1\%$; $N = 8.87\%$.

l, Tris o,Phenanthroline Osmium II Perchlorate Monohydrate.

The filtrate from the precipitation of d, tris o,phenanthroline osmium II d,antimonyl tartrate (*vide supra*) was treated with sodium perchlorate solution and the resulting precipitate of the lævo-perchlorate crystallized several times from hot water with the addition of sodium perchlorate.

A 0.003% solution in water gave $\alpha = -0.10_7°$ (1 dm. tube) whence $[\alpha]_{5461}^{25} = -3570°$ and $[M]_{5461}^{25} = -33,800°$.

Found : $Os = 19.7\%$; $N = 8.95\%$.

Calculated for $Os(C_{12}H_8N_2)_3(ClO_4)_3.1H_2O$: $Os = 20.1\%$; $N = 8.87\%$.

SUMMARY.

Tris o,phenanthroline osmium II iodide was prepared by reaction between o,phenanthroline and ammonium bromosmate in glycerol solution at 250–270° C., followed by dilution with water and addition of potassium iodide. The intensely greenish brown solutions containing the ion $Os(phenan)_3^{++}$ are reversibly oxidized to the red $Os(phenan)_3^{+++}$ at approximately 0.9 volt. The enanthiomorphous forms were isolated through the antimonyl tartrates, and the active perchlorates gave $[M]_{5461}^{25} = +34,800°$ and $-33,800°$.

ACKNOWLEDGEMENTS.

REFERENCES.

Burstall, Dwyer and Gyarfas, 1950. *J. Chem. Soc.*, 953.
Dwyer and Gyarfas, 1949. THIS JOURNAL, **83**, 174.
——————————— 1950. *J. Am. Chem. Soc.* In Press.
Dwyer, Humpoletz and Nyholm, 1946. THIS JOURNAL, **80**, 212.

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ON THE GRADING OF DUNE SANDS NEAR CASTLEREAGH, NEW SOUTH WALES.
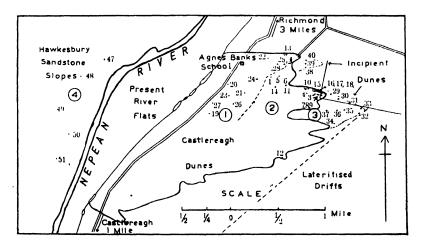
By D. S. SIMONETT, M.Sc.

With one map and three text-figures.

In the western part of the Sydney Plain near the Nepean River at Castlereagh lies a small field of fixed longitudinal sand ridges.   In an earlier paper (Simonett, 1949) it was concluded that these dunes were built up by westerly winds with sands derived from the Hawkesbury sandstone soils west of the Nepean ; and that sand movement followed vegetation destruction on the sandstone, probably during the Early Recent arid period.   It is now proposed to discuss the changes in grading wrought on the source soils during the dune building.

Crest and trough samples (33) were taken from the western and eastern parts of the dunes, respectively removed about 1½ and 2½ miles from the source. Five source soil samples were collected, together with 13 from the " Incipient Dunes ", built up in advance of the main sand movement and composed of finer sands.   The location of the samples is given in Map 1.
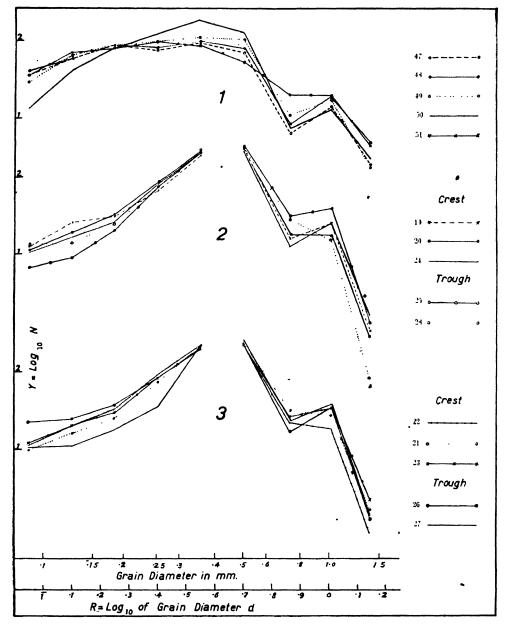
All the analyses obtained by dry sieving* were plotted graphically to enable ready comparisons of grain-size gradings ; of these, 36 representative samples have been selected and plotted on a series of seven graphs.

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* 100 grm. samples were taken, organic matter destroyed by boiling with hydrogen peroxide, and after thorough dispersion and decantation of particles smaller than 0·02 mm. the sands were oven-dried and sieved in a nest of Tyler sieves for 15 minutes on a Tyler " Ro-Tap " sieving machine.   The following meshes were used (apertures in millimetres) :

14 (1·168) ; 20 (0·888) ; 28 (0·589) ; 35 (0·417) ; 48 (0·295) ; 65 (0·208) ; 100 (0·147) ; 150 (0·104) ; 200 (0·074).
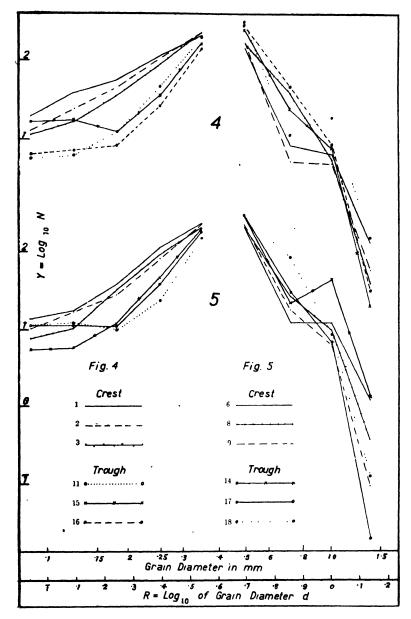
Bagnold's (1941) method of plotting these results was selected† for, using it he found that in naturally wind-blown sands " outside a definite central zone the grades to right and left of the peak (diameter) fall off each at its own constant rate ". To those wind-blown sands whose grading conformed to this simple

arrangement of two straight lines inclined upwards, meeting at an apex, the top of which was replaced by a small arc, he applied the term *regular sands* whether the arrangement was symmetrical about the peak or not (*loc. cit.*, p. 118).
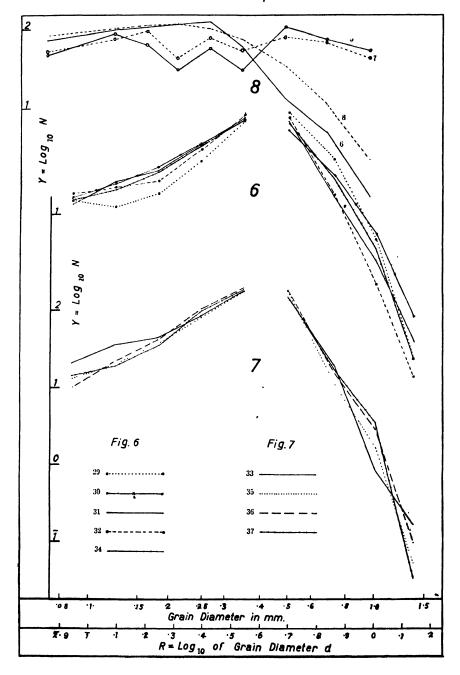
† The logarithm of the percentage-weight of sand per unit of the log. diameter scale is plotted as ordinate against an abscissa of the log. grain diameter.

Considering the grading of each group. The five source samples plotted in Figure 1 show the same characteristic grading, the most distinctive features of which are the marked irregularity on the coarse side and the gentle fall away from the peak on the fine side with a slight steepening to the finest grades.

The western group of sands, Figures 2 and 3, moved a mile to $1\frac{1}{2}$ miles, have altered in grading to approach regularity, particularly about the peak diameter, but on the coarse side the initial excess of sands of the range 0·888–1·16 mm. over that of 0·589–0·888 has been but tardily removed·(only samples 22, 24 (crest) and 28 (trough) show any significant reduction) and these are the eastern-most samples of this group. The steepening in the finest grades of the parent

sand has, however, not only been removed, but has been replaced by a slight flattening in the trough samples. Other than this little difference in crest and trough grading is evident at this stage.

Fig. 6

29	••••••••••
30	—•—
31	————
32	•––––•
34	————

Fig. 7

33	————
35	•••••••••
36	– – – –
37	————

Grain Diameter in mm.

$R = Log_{10}$ of Grain Diameter d

$Y = Log_{10} N$

In the eastern sands (a further half to one mile removed from the source), Figures 4 and 5, the changes which were barely evident in the western analyses are pronounced, and a considerable difference in trough and crest grading is to

be seen, the finer sands collecting on the ridges and coarse sands in the troughs. From all the crests the excess of the penultimate grade over that retained on sieve 28 has been eliminated ; but the curve is still kinked at this point.   On the other hand in only those trough samples farthermost from the source has this occurred.*

The crest sands are near-regular on both fine and coarse sides of the grading but the trough samples are not, for the slight flattening in the finest grades in the trough samples of the western sands is now very marked in the eastern trough sands.

The " Incipient Dunes " sands are essentially regular and lack both the coarse side distortion and the fine side flattening of the true sand dunes (Figures 6 and 7).

DISCUSSION.

It seems evident from the analyses that although the rate of removal of the initial distortion in the coarse grading of the source soils differed slightly in the crest and trough samples (the former approaching regularity a little earlier than the troughs) both required between two and three miles transport for such removal.

These results are interesting when compared with work along similar lines by Bagnold (1941) and Chepil (1946).

Bagnold (1941, 142–3), working with a regular sand distorted in the ultimate fine and coarse grades by the addition of excess sand, found in the wind tunnel that the excess in the finest grades was " hardly (removed) at all in the accretion deposits " by wind action, whilst that on the coarse-side was rapidly removed. On the basis of this experiment he concluded that " the processes . . . which tend to produce the logarithmic relation between the proportion by weight and the grain diameter, are different on the fine and coarse sides of the grading, though both must occur in the early part of the cycle of movement ".

Chepil (1946), working in the Canadian Wheat Belt, analysed sands piled into small dunes resulting from drift from eroding cultviated fields of a quarter to half a mile in length.   He found that " except for a few slight kinks, the two arms of each curve are straight lines and agree, at least in essential features, with the grading diagrams found by Bagnold for desert sand.   Such marked and consistent grading of drift material seems almost incredible in view of the fact that the materials deposited in dunes were in the majority of cases the result of a single dust storm " and concluded that " a distance (of a quarter to half a mile) was apparently sufficient for effecting an ultimate selection of the blown materials ".

A greater distance was needed to remove the coarse-side distortion at Castlereagh than would have been expected on the basis of Bagnold's and Chepil's results.   Comparing the diameter of the Castlereagh distortion (1·0 mm.) with the latter (0·5–0·65 mm.) an even earlier removal than Chepil's might have been expected.   Clearly some factor must have retarded the sorting.   In part the discrepancy with Bagnold's experiment (loc. cit., pp. 142–3) may be explained by his use of a regular source sample distorted only in the ultimate grades ; i.e. one which would reach regularity very quickly.   However, this argument cannot apply to Chepil's irregular source samples (Figure 8).   It is more likely that the answer lies in the amount of sand in movement, the speed of sorting depending on the continuity of supply of irregular sand from up-wind.   With

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* With the exception of the most easterly trough samples from which the irregularity has been shifted (16, 17, 18) all the trough samples retain the irregularity to a greater degree than crest samples moved an identical distance.   The following pairs of trough and crest samples have been moved the same distance : all are less regular in the troughs than the crests :

4C : 10T ; I, 5 : 14 ; 6 : II ; 3 : 15 ; 2 : 13.

large volumes of sand available for movement fresh sand containing the coarse-side irregularity would continually be moving over the areas in which this coarse-side excess remained as residuals from earlier movement emphasizing the irregularity and in effect shifting the removal-bed down wind. All the evidence at Castlereagh points to large volumes of sand available (Simonett, 1949), a situation far less likely in the heavier wheat soils studied by Chepil. The similarity of grading of " Incipient Dune " sample 39 moved half a mile less than the other samples of Figure 6 (see also Map 1) supports this view. It is possible that with certain initial gradings and large masses of sand for transport the attainment of regularity may be even longer delayed than at Castlereagh.

The significance of the marked flattening in grading in the finest sands of the eastern trough samples is not easily determined. We cannot regard it as an unremoved initial irregularity, for the reverse was the case in the parent sand where the grading steepened slightly to the finest grades. It is clearly a feature produced on movement and appears to be fundamental to at least the early process of grading of the trough samples.

The suggestion is made that this flattening, which it will be seen occurs in sieves 150 (0·104–0·147 mm.) and 200 (0·074–0·104 mm.), may be due to the fact that about this diameter (0·08 mm., Bagnold, *loc. cit.*, p. 88) the fluid threshold for grain movement is closest to the impact threshold, and thus particles of diameter 0·10–0·15 mm. (Chepil, 1945, p. 404) are the most readily eroded and maintained in saltation of all grades. Thus with greater wind sorting at the crests any excess of the fine grades would tend to be directed outwards to the troughs, where decline in wind velocity would favour deposition.

The concentration of fine grades of this diameter in the troughs is interesting when compared with the peak diameters of the crest and trough sands of the Simpson Desert seif dunes analysed by Carroll (1944) and Crocker (1946). They found that the coarsest sands collected on the crests (peak 0·17 mm., one 0·35 mm.) and the finest in the troughs (peak 0·85–0·9 mm.). On the other hand at Castlereagh the eastern crest sands (peak load-sieve 48/0·295 mm. 31–36%) are finer than the trough sands (peak load sieve 35/0·417 mm.45–53%). Bagnold (*op. cit.*, p. 228) found the fine-crest-coarse-trough relationship to be characteristic of the Libyan seif dunes and postulated it as general. Crocker (1946) suggested that the reversal of the relationship in the Simpson Desert sands may be due to their extreme fineness and their concentration about the critical diameter of 0·08 mm. They are undoubtedly much finer than the Castlereagh sands or all the examples Bagnold gives of typical Libyan Desert gradings.

On the evidence available at Castlereagh we cannot say that the extreme fine-side distortion of the eastern trough sands is more than a feature of the early part of the process of grading. However, the fact that the fine-side distortion in the Castlereagh trough samples occurs in the same diameter range as the peak diameter of the Simpson Desert trough samples suggests that it is more than an early phase in the grading cycle and may be in fact fundamental to the whole process. The reason for the concentration of these grades (0·08–0·15 mm.) in the troughs appears to be bound up with the ease with which they are moved ; gentle winds in particular capable only of moving sand on the crests would ensure their selective migration to the troughs.

Madigan (1946, p. 62) suggested that the concentration of these grades in the troughs in the Simpson Desert was a post dune-fixation phenomenon—" the higher percentage of fine grades and clay particles in the two inter-ridge samples as compared with crests is probably due to the winnowing effect on the crests, where under present conditions of no set lateral movement and secondary winds from both sides the coarser fractions will tend to remain as residuals on the crests and the crest sand to become more regular than that in the lanes. The

" smoking " effect in strong lateral winds will carry the dust and fine particles well down into the lee of the ridge, where it will remain ".   This process can equally well take place during the dune-building and may be regarded as a normal dune process.

With wide source sample gradings double maxima (one fine 0·08 mm., and one coarse) should occur in the gradings of the lower slopes of seif dune plinths in young deserts where the dunes are closely spaced.   Thus in the grading of sands from the Kalahari longitudinal dunes analysed by Lewis (1936) (Table 1) the concentration of sands finer than 0·15 mm. in the lower slopes and troughs is marked.   The tendency to another peak in these gradings coarser than the peak of the crest gradings is also evident.*   On the other hand with narrow source sands one or other of the maxima would be damped.   The Simpson Desert sands are low in coarse grains and lack a definite coarse maximum in the troughs.

Geological time must be considered as a factor affecting gradings.   In young dune fields (Kalahari) with low, closely spaced dunes, fine grades will mantle the lower dune slopes as well as the troughs ; but in old seif dune fields long continued winnowing of steep-sided massive dunes, miles apart as in Libya, would move all the fine grades into the sand sheet between the dunes.   An uncomplicated fine-crest-coarse-lower-slope grading relationship as described by Bagnold would result on the dunes, the intervening sand plain consisting of the very fine grades and residual very coarse grades.

No one simple general rule can characterize either rate of removal of irregularities or the grading relationships on dunes.   It may be misleading to apply results obtained from wind-tunnel and field tests on removal of irregularities, where sands were driven away from a source area, to desert areas such as the Simpson where Madigan has shown that many of the dunes arose *ab initio* from a sand sea.   Equally, grading relationships on seif dunes will be a function of origin (*ab initio* dunes or dunes trailing from a windward source) grading of the source sands, and maturity of the dune system.   The attempt above to indicate the general types of gradings that are likely to occur in a limited group of circumstances must be considered speculative ; a generalized theory of dune grading must, however, take all the factors considered above into account.

SUMMARY

The rate of removal of irregularities on the coarse side of the grading appears to vary with the amount of sand in movement.   Concentration of grades of the diameter range 0·08–0·15 mm. in the troughs of the Castlereagh longitudinal dunes and also in the troughs of desert young seif dune fields (Kalahari, and Simpson deserts) appears to be a normal feature of the grading of closely spaced seif dune fields.   Grading relationships on longitudinal dunes will be a function of the maturity of the system, the width of the grading of the source sands, and the origin of the dunes (*ab initio* dunes arising in a sand sea, or dunes trailing from a limited windward source).

ACKNOWLEDGEMENTS.

* The results given in Table 1 (appendix No. 1 of Lewis's paper) are mean analyses.   About 200 samples were analysed from ten localities for crests, slopes and corridors of the dunes.   Thus 30 groups of means are available, about six samples to a mean, assuming uniform sampling from all localities.   This lumping of analyses together must make one suspicious of the value of Lewis's results.   However, since all ten groups possess roughly similar gradings, a certain amount of value may be given to them, though they must be used with caution.

TABLE 1.

(After Lewis, 1936.)
Mechanical Analyses of Sands.
Kalahari Sand Dunes.
Mean of all Readings.

Percentages by weight retained on each sieve.

14	28	40	48	65	90	115	150	Passing 150	Remarks.
				1. Houmoed.					
—	—	5	15	29	19	14	9	9	Slopes.
—	—	2	21	44	20	9	3	1	Crests.
2	5	10	9	16	15	13	12	18	Straats.
				2. Lentlands Pan.					
—	—	1	8	29	24	22	9	7	Slopes.
—	—	—	10	42	28	14	4	2	Crest.
—	—	6	19	27	18	15	7	8	Staat.
				3. Kakolk.					
—	—	5	7	20	22	18	16	12	Slopes.
—	—	4	22	31	21	12	7	3	Crest.
—	8	16	6	10	12	13	14	21	Staat.
				4. Abiquas Puts.					
—	—	1	3	21	17	28	13	17	Slopes.
—	—	—	4	25	25	24	13	9	Crest.
—	—	2	3	12	11	17	18	37	Straat.
				5. Albion.					
—	2	12	9	16	18	18	12	13	Slopes.
—	—	6	13	27	23	18	9	4	Crest.
3	2	9	9	17	18	17	11	14	Straat.
				6. Gemsbok Plains.					
—	—	2	17	38	19	14	6	4	Slopes.
—	—	1	14	41	22	13	6	3	Crest.
—	2	9	21	25	13	12	8	11	Straat.
				7. Bushmans Puts.					
—	1	6	10	20	17	19	13	14	Slopes.
—	—	2	8	25	22	21	12	10	Crest.
—	3	10	11	17	14	17	12	16	Straat.
				8. Tellery Pan.					
—	—	1	7	21	22	22	16	11	Slopes.
—	—	2	13	32	22	17	10	4	Crest.
—	1	6	10	18	16	16	17	16	Straat.
				9. De Hoek.					
—	—	3	6	22	21	23	12	13	Slopes.
—	—	—	6	40	24	21	6	3	Crest.
—	2	7	6	14	15	20	16	20	Straat.
				10. Debinga.					
—	5	15	9	10	11	19	16	15	Slopes.
—	2	10	11	13	13	23	17	11	Crest.
2	12	16	6	7	8	18	15	16	Straat.

Sieve apertures in mms. are as below :
14 (1·168), 28 (0·589), 40 (0·381), 48 (0·295), 65 (0·208), 90 (0·150), 115 (0·124), 150 (0·102).

REFERENCES.

Bagnold, R. A., 1941. The Physics of Blown Sand and Desert Dunes. Methuen, London.

Carroll, D., 1944. The Simpson Desert Expedition, 1939, Scientific Reports. No. 2, Geology—Desert Sands. *Trans. Roy. Soc. S. Aust.*, **68**, 1, 49.

Chepil, W. S., 1945. Dynamics of Wind Erosion. II. Initiation of Soil Movement. *Soil Sci.*, **60**, 397.

——————— 1946. Dynamics of Wind Erosion. VI. Sorting of Soil Material by the Wind. *Soil Sci.*, **61**, 331.

Crocker, R. L., 1946. The Soil and Vegetation of the Simpson Desert and its Borders. *Trans. Roy. Soc. S. Aust.*, **70**, 2, 235.

Lewis, A. D., 1936. Sand Dunes of the Kalahari. *S.A. Geog. Journ.*, **19**, Dec. 22.

Madigan, C. T., 1946. The Simpson Desert Expedition, 1939. Scientific Reports, No. 6, Geology—The Sand Formations. *Trans. Roy. Soc. S. Aust.*, **70**, 1, 45.

Simonett, D. S., 1949. Sand Dunes near Castlereagh, New South Wales. *Aust. Geog.*, **5**, 8, 3.

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THE CHEMISTRY OF OSMIUM.

PART V. THE REDOX POTENTIALS OF THE TRIS 2 : 2'-DIPYRIDYL OSMIUM II/III AND THE TRIS O,PHENANTHROLINE OSMIUM II/III COUPLES.

By F. P. DWYER, D.Sc.,

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and (MISS) E. C. GYARFAS, M.Sc.

Tris 2 : 2' dipyridyl osmium II salts and analogous o-phenanthroline compounds (Burstall, Dwyer and Gyarfas, 1950 ; Dwyer, Gibson and Gyarfas, 1950) are reversibly oxidized to the corresponding osmium III complexes. The potentials of the two reactions have now been determined in order to complete the iron, ruthenium and osmium triad of such complexes, as well as to ascertain the suitability of the compounds as redox indicators.

The oxidized form of the dipyridyl compound was sufficiently stable to be obtained in solution in known concentration, hence the potential could be obtained by the standard method of allowing an electrode to come to equilibrium in an equimolar mixture of oxidant and reductant. The oxidized form of the phenanthroline complex, however, was unstable and rapidly underwent reduction. This reaction has already been noted with the oxidized forms of the iron and ruthenium complexes with o-phenanthroline (Dwyer and McKenzie, 1947 ; Dwyer, Humpoletz and Nyholm, 1946). The potential of the phenanthroline complex was determined by exactly half oxidizing a standardized solution of the reduced form and observing the maximum potential attained on an electrode (Dwyer, 1949).

Both systems were typically cationic, the potentials decreasing with increasing ionic strength. At the same ionic strengths, the potentials of the phenanthroline complex were slightly higher. This follows the same trend as with the iron and ruthenium compounds. However, unlike the Fe and Ru compounds, the stability of the oxidized form decreased with increasing acid concentration.

With the completion of the potential investigations of the 2 : 2' dipyridyl and o-phenanthroline complexes with the members of the iron triad, it is interesting to compare the potential changes consequent upon complex formation. The figures shown in detail in Table I are approximate, since corresponding potentials of the simple bivalent/trivalent system and the bivalent: trivalent complex system are not available in some instances at the same ionic strength. The maximum potential change occurs with the ruthenium compounds, from $+0\cdot085$ volt for the Ru^{++}/Ru^{+++} couple to $1\cdot31$ volt for the $Ru(phenan)_3{}^{++}/Ru(phenan)_3{}^{+++}$ system, a change of $1\cdot225$ volts. The potential change consequent upon the formation of the osmium compounds cannot be stated with any degree of accuracy. The potential of the system Os^{++}/Os^{+++} is unknown, and probably cannot be determined directly, since disproportionation of the Os^{++} ion can be expected to occur. With an estimated value of $-0\cdot25$ volt, the change is of the order of $1\cdot13$ volts for the formation of the phenanthroline complex.

TABLE I.

	Potential M++/M+++.	Potential Dipyridyl Complex.	Potential Change.	Potential Phenan. Complex.	Potential Change.
Fe	+0·75 V.[1]	+1·096 V.[2]	0·346 V.	+1·120 V.[2]	0·370 V.
Ru	+0·085[3]	+1·30[4]	1·315	+1·31[4]	1·325
Os	−0·25[5]	+0·878	1·128	+0·877	1·127

[1] Thermodynamic value, 0·771 V. (Latimer, 1940.)
[2] Dwyer and McKenzie, 1947.
[3] Backhouse and Dwyer, 1949.
[4] Dwyer, 1949.
[5] Estimated value.

Two general observations are noteworthy : the stability of the reduced form is the greater with phenanthroline ; and of the oxidized form with dipyridyl. The iron compounds in both oxidized and reduced states are less stable chemically and optically than the ruthenium and osmium compounds.

EXPERIMENTAL.

The redox potential determinations were carried out at 25° C. in the apparatus used for previous determinations (Dwyer, McKenzie and Nyholm, 1940). The saturated calomel electrode was calibrated against quinhydrone in potassium hydrogen phthalate solution, pH 4·00, using a gold electrode. The value of the potential accepted for the latter electrode was 0·4623 V. at 25° C. The equimolar solutions of tris 2 : 2′ dipyridyl osmium II and osmium III perchlorates were prepared by making 0·001 M solution of the reductant, dividing into two portions, and oxidizing one portion with a slight excess of chlorine. The excess chlorine was then expelled by a rapid current of air saturated with water. The absence of chlorine was shown by taking 10 ml. of the pink oxidized solution and adding one drop of the deep green reduced solution. The consequent colour change showed that chlorine was absent. Equal volumes of the oxidized and reduced solutions were then mixed. Water and acid were subsequently added, so that the final solution was M/4000 with respect to oxidant and reductant ion.

The tris o-phenanthroline osmium II perchlorate was prepared in saturated aqueous solution, approximately M/1300, diluted with water and acid to twice the volume, and potentiometrically titrated with 0·01 N potassium permanganate, or in the first determination (with no added acid), with dilute chlorine water. The volume of permanganate needed to half oxidize the solution was thus obtained. Immediately following, another solution was prepared with added acid and water and the calculated volume of permanganate so that the concentration of oxidant and reductant was M/5200 each. A platinum electrode in the mixture was read each minute until the maximum value was obtained. For acid concentrations of 0·05 N and 0·1 N the maximum was stable for more than one and a half hours. With stronger acid the time of duration of the maximum decreased, so that with 1 N acid the potential commenced to fall in the first minute.

With the osmium dipyridyl system, the potential was stable for some hours up to an acid concentration of 1 N, when a decrease of 35 mV. occurred in fifteen hours. With the stronger acid concentrations 2 N, 3 N and 5 N, the potentials decreased after a few minutes. The potentials observed are shown in Table II.

TABLE II.

Acid Conc. (Normality).	Os(dipy)$_3$$^{++}$/Os(dipy)$_3$$^{+++}$	Os(phenan)$_3$$^{++}$/ Os(phenan)$_3$$^{+++}$
None added	0·877$_7$ V.	0·877 V.
0·05	0·863$_1$	0·863$_7$
0·1	0·855$_7$	0·859$_3$
0·2	0·847$_3$	0·856$_4$
0·5	0·833$_1$	0·842$_1$
1·0	0·819$_7$	0·822$_5$
2·0	0·802	—
3·0	0·775	—
5·0	0·727	—

SUMMARY.

The redox potentials of the two systems tris 2 : 2′ dipyridyl osmium II/ tris 2 : 2′ dipyridyl osmium III, and tris o-phenanthroline osmium II/tris o-phenanthroline osmium III have been determined. Both systems were found to be typically cationic. The potentials respectively in 0·1 N hydrochloric acid were 0·8557 and 0·8593 volt.

REFERENCES.

Backhouse, J. R., and Dwyer, F. P., 1949. THIS JOURNAL, **83**, 138.
Burstall, F. H., Dwyer, F. P., and Gyarfas, (Miss) E. C., 1950. *J. Chem. Soc.*, **953**.
Dwyer, F. P., Gibson, N. A., and Gyarfas, (Miss) E. C., 1950. THIS JOURNAL, **84**, 68.
Dwyer, F. P., and McKenzie, H. A., 1947. *Ibid.*, **81**, 93.
Dwyer, F. P., Humpoletz, J. H., and Nyholm, R. S., 1946. *Ibid.*, **80**, 212.
Latimer, W. M., 1940. " Redox Potentials." Prentice Hall, New York.

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THE CHEMISTRY OF OSMIUM.

PART VI. THE USE OF TRIS O,PHENANTHROLINE OSMIUM II PERCHLORATE AS AN INTERNAL REDOX INDICATOR.

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The first internal redox indicator for the titration of ferrous iron with potassium dichromate was diphenylamine (Knop, 1924). Analogous compounds—diphenylamine sulphonic acid and diphenyl benzidine—have been recommended in order to overcome the relatively diffuse end-point and poor stability of prepared solutions of the diphenylamine reagent. The redox potential of all of these indicators is approximately 0·8 volt—hence the normal ferrous/ferric potential (0·7 volt) must be lowered by the addition of phosphoric acid or sodium fluoride in order to prevent the overlapping of the potentials of the indicator and the iron system. Tris 2 : 2' dipyridyl ferrous sulphate and later tris o-phenanthroline ferrous sulphate were recommended by Walden, Hammett and Chapman (1931) as more suitable reagents. In strongly acid solution (approximately 4 normal) the redox potentials of these indicators are 0·92 and 1·03 volt, and the titration of both the ferrous iron and the indicator can be carried to completion. The reduced form of the indicator, however, is unstable in acid of such high concentration, and the disappearance of the red colour of the indicator, which signalises the end of the titration, can well be due to decomposition. In solutions of lower acid concentration, the maximum potential available from the dichromate is insufficient to effect the complete oxidation of the indicator, the potential of which is higher in weakly acid solution (1·102 volts in 0·1 N acid ; Dwyer and McKenzie, 1947). A number of substituted dipyridyl complexes with ferrous iron were recently prepared by Smith (1949), who suggested that the ideal redox indicator for the ferrous/dichromate titration should have a potential of 0·85 volt.

Tris 2 : 2' dipyridyl osmium II perchlorate and the corresponding o-phenanthroline compound have been shown recently to be reversibly oxidized at a potential of 0·86 volt in 0·1 N acid (Dwyer, Gibson and Gyarfas, 1950). The colour changes accompanying oxidation were intense green to pink and intense brown to pink respectively. The conditions for the use of these substances as indicators for the ferrous/dichromate titration were determined by the standard procedure of carrying out mixed potentiometric titrations of ferrous sulphate and each of the osmium complexes as the perchlorate in sulphuric acid of varying concentrations.

The titration in 0·1 N acid gave a satisfactory end point " break " for the iron titration system, but not for either of the indicators (Fig. 1a). Both the ferrous/ferric and the osmium II complex/osmium III complex systems are cationic and the potentials fall with increasing ionic strength—but the decrease is greater with the osmium complex system and as a result·both systems tend to merge. By the addition of either phosphoric acid or sodium fluoride in 1 N acid, both of these systems were satisfactorily separated.

It is to be noted that since the reduced form of the indicator is very much darker than the oxidized form, the visual end point does not coincide with the potentiometric end-point, but is about 30 to 50 mV. higher.
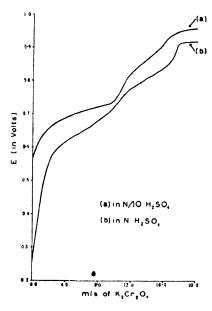
Fig. 1.
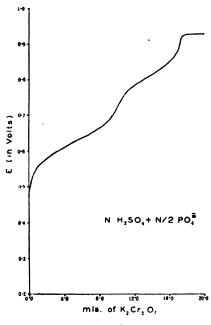
Fig. 2.

Under the latter conditions both osmium complexes were shown to be satisfactory indicators from the point of view of the potential. However, the

colour change of the tris 2 : 2' dipyridyl compound in the presence of chromium sulphate from deep green to a paler green was difficult to detect. The colour change of the o-phenanthroline complex from yellow-green to blue-green was well marked and easily detected.

In titrations involving $0 \cdot 01$ N potassium dichromate, the end point was diffuse, but excellent with the $0 \cdot 1$ N reagent. From a series of titrations it was found that with tris o-phenanthroline osmium II perchlorate the mean error was $0 \cdot 1\%$.

EXPERIMENTAL.

The Potentiometric Titration of Ferrous Sulphate and the Complex Osmium II Perchlorates.

The titrations were carried out at 25° C., with a bright platinum electrode in the redox assembly used in previous work (Dwyer, McKenzie and Nyholm, 1944). The ferrous sulphate solution (10 ml., $0 \cdot 01$ N) was mixed with the indicator solution (100 ml., $0 \cdot 01$ M Os(dipy)$_3$(ClO$_4$)$_2$H$_2$O, or $0 \cdot 0078$ M Os(phenan)$_3$(ClO$_4$)$_2$H$_2$O), and the required volume of sulphuric acid (10 N). The potassium dichromate ($0 \cdot 01$ N) also contained the same concentration of sulphuric acid. Typical curves are shown in Figs. 1a, 1b and 2.

The Estimation of Ferrous Iron with Tris o,Phenanthroline Osmium II Perchlorate as Indicator.

Various volumes of standard ferrous sulphate solution were diluted with sulphuric acid so as to produce approximately 100 ml. of normal acid solution. Syrupy phosphoric acid (3 ml.) was added, and saturated ($0 \cdot 0078$ M) tris o-phenanthroline osmium II perchlorate (2 ml.). The mixture was titrated with standard $0 \cdot 1$ N potassium dichromate solution. For comparison, the titration was carried out also with diphenylamine solution (1%) as internal indicator, using the recommended procedure (Vogel, " A Text Book of Quantitative Inorganic Analysis ", Longmans, Green & Co., London, 1947). The results are summarized in Table 1.

TABLE I.

Mass Fe Taken.	Fe Found (Os-(phenan)$_3$(ClO$_4$)$_2$).	Percentage Error.	Fe Found (Diphenylamine).	Percentage Error.
$0 \cdot 0692$ g.	$0 \cdot 0690$ g.	$-0 \cdot 3$	$0 \cdot 0701$ g.	$+1 \cdot 3$
$0 \cdot 1039$ g.	$0 \cdot 1039$ g.	$0 \cdot 0$	$0 \cdot 1047$ g.	$+0 \cdot 8$
$0 \cdot 1385$ g.	$0 \cdot 1388$ g.	$+0 \cdot 2$	$0 \cdot 1393$ g.	$+0 \cdot 6$
$0 \cdot 1731$ g.	$0 \cdot 1731$ g.	$0 \cdot 0$	$0 \cdot 1739$ g.	$+0 \cdot 5$
$0 \cdot 2077$ g.	$0 \cdot 2077$ g.	$0 \cdot 0$	$0 \cdot 2088$ g.	$+0 \cdot 5$
$0 \cdot 2770$ g.	$0 \cdot 2770$ g.	$0 \cdot 0$		
$0 \cdot 3462$ g.	$0 \cdot 3459$ g.	$-0 \cdot 1$		
		Mean $0 \cdot 1\%$		Mean $+0 \cdot 7\%$

SUMMARY.

Tris o-phenanthroline osmium II perchlorate is recommended as an internal redox indicator for the determination of ferrous iron with potassium dichromate. The reagent, used in the form of its saturated aqueous solution, is stable. The titration is performed in normal acid solution in the presence of phosphoric acid. An accuracy of $\pm 0 \cdot 1\%$ is obtained.

REFERENCES.

Brandt, W. W., and Smith, G. F., 1949. *Analytical Chem.*, **21**, 1313.
Dwyer, F. P., and McKenzie, H. A., 1947. THIS JOURNAL, **81**, 93.
Dwyer, F. P., Gibson, N. A., and Gyarfas, (Miss) E. C., 1950. *Ibid.*, **84**, 68.
Dwyer, F. P., McKenzie, H. A., and Nyholm, R. S., 1944. *Ibid.*, **78**, 260.
Knop, J., 1924. *J. Am. Chem. Soc.*, **46**, 263.
Walden, G. H., Hammett, L. P., and Chapman, R. P., 1931. *J. Am. Chem. Soc.* **53**, 3908.
Vogel, A., 1947. " A Text Book of Quantitative Inorganic Analysis ", Longmans, Green & Co.,
    London.

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THE ESSENTIAL OIL OF *BÆCKEA CRENULATA* (DE CANDOLLE).

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The botany of this Myrtaceous shrub is described in Bentham's " Flora Australiansis ", Vol. 3, pages 71–78. It is a small heath-like shrub with nearly round leaves about ¼ in. long, the edges of which are minutely crenulate. They grow in irregular fashion around the stem, and give to the plant a distinctive appearance. The plant, which has small white to pink flowers, occurs in patches along the coast of New South Wales into Queensland, and on the Blue Mountains of New South Wales. At one time it was very plentiful on most of the headlands of our popular seaside resorts, extending from Broken Bay in the north to Ulladulla in the south. Some of the localities between the north head of Port Jackson and Cronulla, where collections were made during the past quarter of a century, have since been cleared for building purposes. A pleasant odour of terpenes, modified by linalool, is readily detected on crushing the leaves between the fingers.

ESSENTIAL OIL.

Although the essential oil was examined first in 1921, its investigation has been continued to the present time. Little difficulty was experienced in isolating and identifying the principal terpenes, but the authors suspected others which have defied identification. Repeated efforts, using fresh samples of oil distilled from material collected from widely different localities during the past 27 years, have merely confirmed the original results. Quite recently, fresh samples of oil were distilled, but notwithstanding the use of improved methods of fractional distillation, no additional terpene constituents could be identified. It was possible, however, by the use of the Lecky-Ewell and Bower-Cooke fractionating columns, to isolate and identify the alcohol linalool, whose presence, although previously suspected, had not been established beyond doubt.

The essential oils from all consignments, obtained in yields of $0 \cdot 2\%$ to $0 \cdot 36\%$, varied in colour from a lemon tint to deep brownish yellow, and possessed a pleasant, characteristic odour of the principal terpene constituents, modified by that of the alcohol, linalool. The corks of the containing vessels were readily bleached. On standing, many of the oils deposited yellow prismatic crystals of the phenol ether bæckeol, $C_{13}H_{18}O_4$, m.p. 103–104°.

Although bæckeol has been found in other Australian essential oils (Penfold, 1925) it was first isolated from the essential oil of *B. crenulata* in 1922 (Penfold and Morrison, 1922). The chemical deportment and constitution of this unique substance were described in a further communication to the Society in 1937 (Penfold and Morrison, 1937). Bæckeol was synthesised simultaneously by two groups of workers in 1940 (Ramage and Stowe, 1940 ; Hems and Tod, 1940).

The principal constituents, which have so far been identified, are as follows, viz. : *d*-α-pinene, *d*- and *dl*-limonene, γ-terpinene, cymene, linalool, sesqui-terpenes and bæckeol.

Bæckea crenulata (De Candolle).

Date.	Localities (in New South Wales).	Weight of Leaves. Lb.	Yield of Oil. %	d 15°/15°	α20D	n20D	Solubility in 80% Alcohol. (W/W.)	Ester Number 1½ hours Hot Sap.	Ester Number after Acetylation.	Remarks.
1921	Waverley	7	0·2	0·8606	+15°	1·4777	10 Vol.			3 g. Bæckeol recovered after collection of oil.
20/3/1922	Long Bay	108¾	0·2	0·8923	+28·65°	1·4800	8 Vol.			
7/2/1933	Ulladulla	150	0·32	0·8704	+25·8°	1·4776	7 Vol.	12·7	47·6	
8/8/1934	Ulladulla	212	0·2	0·8778	+21·85°	1·4813	10 Vol.	11·5	46·7	
3/2/1936	Malabar	196	0·28	0·8995	+24·8°	1·4830	8 Vol.	28·6	87·2	
9/8/1938	Ulladulla	226	0·28	0·8735	+27·63°	1·4773	9 Vol.	11·0	43·6	
23/9/1940	Ulladulla	309	0·31	0·8690	+29·0°	1·4752	9 Vol.	13·0	43·0	2·5 g. Bæckeol recovered after collection of oil.
8/5/1941	Curl Curl	418	0·36	0·8690	+26·66°	1·4773				
11/10/1944	Wattamolla	60	0·33	0·8799	+12·27°	1·4822	9·0 Vol.	11·5	39·0	
22/10/1947	Wattamolla	378	0·3	0·8634	+17·46°	1·4779	8·5 Vol.	10·0		
20/7/1948	Malabar	468	0·23	0·8733	+19·5°	1·4787	Insol. 10 Vol.	27·0	69·0	

EXPERIMENTAL.

A total of 2532 lb. of leaves and terminal branchlets was subjected to distillation in steam, and yielded crude oils possessing physical and chemical constants shown in the table.

The oil obtained from each consignment of foliage was separately investigated, but the results of one only have been selected for publication.

200 ml. of oil (Ulladulla sample, 23/9/40) were distilled at 10 mm., viz. :

Fraction.	B.p.	Vol. Ml.	$d \frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
1	To 60°	108	0·8576	+37·1°	1·4718
2	60–65°	52	0·8561	+28·3°	1·4737
3	65–70°	17	0·8592	+19·2°	1·4761
4	Residue	21			

The terpene fractions were allowed to stand over metallic sodium prior to fractional distillation through a Widmer column.

Fraction 1 was fractionated over sodium through a Widmer column at 759 mm. pressure.

Fraction.	B.p.	Vol. Ml.	$d \frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
5	To 159°	6·0	0·8557	+39·2°	1·4676
6	159–162°	12·0	0·8600	+39·7°	1·4682
7	162–164°	19·5	0·8576	+39·5°	1·4686
8	164–168°	27·0	0·8606	+38·6°	1·4706
9	168–175°	29·0	0·8533	+34·8°	1·4736

In view of the similarity of physical constants, fractions 5, 6 and 7 were mixed and fractionated at 760 mm., viz. :

Fraction.	B.p.	Vol. Ml.	$d \frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
10	156–157°	5·5	0·8578	+40·8°	1·4677
11	157–159°	10·0	0·8620	+40·8°	1·4681
12	159–164°	6·5	0·8610	+39·5°	1·4696

Fractions 8 and 9 were mixed with fraction 12, and distilled at 760 mm.

Fraction.	B.p.	Vol. Ml.	$d \frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
12a	159–161°	7·0	0·8601	+39·6°	1·4691
13	161–162°	9·5	0·8596	+39·1°	1·4699
14	162–164°	13·2	0·8590	+38·8°	1·4703
15	164–166°	7·4	0·8550	+38·9°	1·4711
16	166–168°	9·4	0·8519	+37·0°	1·4726
16a	168–178°	11·6	0·8528	+33·2°	1·4767

Fraction 2 was mixed with fractions 16 and 16a and fractionated at 760 mm.

Fraction.	B.p.	Vol. Ml.	$d\frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
16b	169–172°	10	0·8538	+33·1°	1·4746
17	172–173°	13	0·8533	+31·9°	1·4756
18	173–175°	7	0·8529	+30·3°	1·4776
19	175–177·5°	10	0·8510	+28·4°	1·4782
20	177·5–178°	12	0·8511	+25·0°	1·4786
Residue					

Fraction 3 was added to the residue from above distillation, and the mixture fractionated over sodium at 760 mm.

Fraction.	B.p.	Vol. Ml.	$d\frac{15°}{15}$	$\alpha_D^{20°}$	$n_D^{20°}$
21	178–179°	7	0·8526	+22·0°	1·4784
22	179–180°	3	0·8540	+18·0°	1·4776

Determination of d-α-pinene.

Fractions 10, 11 and 12a on further fractionation yielded a specimen of boiling point 155–159°/760 mm., $d_{15}^{15°}$ 0·8610, $\alpha_D^{20°}$ +40·8°. $n_D^{20°}$ 1·4669. Oxidation with potassium permanganate solution gave a good yield of pinonic acid, m.p. 69–70° : $[\alpha]_D^{20°}$ +91·6° ; semicarbazone, m.p. 212°.

Fractions 13 and 14 were oxidised with neutral permanganate solution ; no crystalline product could be isolated. The semicarbazone prepared from the resinous product had m.p. 212°. A mixed melting point with an authentic specimen of pinonic acid semicarbazone showed no depression.

Examination for Presence of Camphene and β-pinene.

Portions of fractions 2 and 15 respectively were oxidised with alkaline potassium permanganate solution, but products indicative of camphene and β-pinene could not be isolated.

Determination of d-limonene and dl-limonene.

A fraction of b.p. 108°/100 mm. had $d_4^{25°}$ 0·8486, $n_D^{25°}$ 1·4803, α_D +31°. Four ml. were dissolved in amyl alcohol (4 ml.) and ethyl ether (8 ml.), cooled at −20°, and bromine (4g.) in ether added slowly. After standing for one hour in a bath of acetone and solid carbon dioxide, a yellow precipitate was obtained (0·9 g.). The precipitate was dissolved in chloroform and reprecipitated with ethyl alcohol at room temperature. This treatment was repeated twice, the crystalline bromide having m.p. 125–126°, unchanged in admixture with an authentic sample of *dl*-limonene tetrabromide ; $[\alpha]_D^{20°}$ ±0° in chloroform.

The original chloroform-alcohol filtrate was cooled with acetone and solid carbon dioxide, a precipitate being obtained, m.p. 98–100°, $[\alpha]_D^{20}$ +46°, in chloroform. Purification with chloroform and ethyl alcohol as above yielded crystals of m.p. 103–4°, corresponding to *d*-limonene tetrabromide.

Determination of γ-terpinene and Cymene.

All fractions boiling above 175°/760 mm., on oxidation with potassium permanganate solution (Penfold, 1925) gave good yields of the erythritol, $C_{10}H_{18}(OH)_4$, m.p. 237–238°, indicative of γ-terpinene.

αδ-dihydroxy-α-methyl-δ-*iso*propylapidic acid, the oxidation product of α-terpinene, was not isolated.

The unchanged oil, on oxidation with hot potassium permanganate solution, yielded *p*-hydroxy*iso*propylbenzoic acid, m.p. 156°, which is indicative of *p*-cymene.

Determination of Linalool.

Portion (0·5 ml.) of a fraction of b.p. 74–80°/10 mm., $d_4^{25°}$ 0·8621, $n_D^{25°}$ 1·4670, α_D +6°, was treated with xenyl carbimide at 100° for one hour. The urethane was isolated and, on repeated recrystallisation from benzene, had m.p. 83–84°.

Sesquiterpenes.

The results of fractionation indicated the presence of sesquiterpenes, but many experiments failed to give crystalline derivatives. Fractions of b.p. 118–123°/10 mm., $d_4^{25°}$ 0·9158, $n_D^{25°}$ 1·4870, α_D +8° and b.p. 123–132°/10 mm., $d_4^{25°}$ 0·9145, $n_D^{25°}$ 1·4835, α_D +12°, respectively, gave the characteristic purple colour in glacial acetic acid solution on treatment with bromine vapour.

SUMMARY.

The oil of *Bæckea crenulata* (De Candolle) found growing on the coast of New South Wales and southern Queensland yields from 0·2% to 0·36% of essential oil containing 85% of terpenes, viz. *d*-α-pinene, *d* and *dl*-limonene, γ-terpinene, cymene, together with linalool (10%), bæckeol, sesquiterpenes, and unidentified constituents.

REFERENCES.

Bower, J. R., and Cooke, L. M., 1943. *Ind. Eng. Chem. Anal. Ed.*, **15**, 290.
Hems, B. A., and Todd, A. R., 1940. *J.C.S.*, 1208.
Lecky, H. S., and Ewell, R. H., 1940. *Ind. Eng. Chem. Anal. Ed.*, **12**, 544.
Penfold, A. R., 1925. THIS JOURNAL, **59**, 351.
Penfold, A. R., and Morrison, F. R., 1922. *Ibid.*, **56**, 87.
——————————————————— 1937. *Ibid.*, **71**, 291.
Ramage, G. R., and Stowe, W. J. I., 1940. *J.C.S.*, 425.
Sutherland, M. D., 1948. *Univ. Queensland Papers in Chem.*, No. 34, 1.

HEARD ISLAND.

GEOGRAPHY AND GLACIOLOGY.

By A. JAMES LAMBETH, B.Sc.

With two Text-figures.

CONTENTS.

GEOGRAPHY.

Early History.

Heard Island appears to have been sighted first by Captain Peter Kemp in 1833 (Mawson, 1935), but it was not until 1853 when it was rediscovered by Captain Heard that the place became generally known. Darwin Rogers, Captain of the *Corinthian*, was the first to land. The island was apparently visited from time to time by sealers but prior to 1947 only four scientific expeditions had called there.

The *Challenger* Expedition (1885) arrived on 5th February, 1873, and a party spent several hours ashore at Corinthian Bay. The German *Gauss* Expedition (Drygalski, 1908) in February, 1902, landed in the vicinity of Atlas Cove. Aubert de la Rue (1929) in 1929 stayed eight days at Atlas Cove, living in a hut erected there by the British Admiralty some years before. In November of the same year the B.A.N.Z. Antarctic Expedition (Mawson, 1932) under the leadership of Sir Douglas Mawson stayed several days at the same place.

On 11th December, 1947, the Australian National Antarctic Research Expedition established a base camp on Rogers Head adjacent to Atlas Cove.

Position of the Island.

Heard Island lies in 73° 30′ E. longitude at 53° 05′ S. latitude, almost halfway between Australia and South Africa. Kerguelen's Land lies about 200 miles to the north-north-west, and the Antarctic Continent—MacRobertson Land—is approximately 1100 miles to the south. The island is approximately 28 miles long and 12 miles broad, the longer axis lying in a N.W.-S.E. direction.

It is the largest member of the McDonald Group, and McDonald Island lies about 27 miles away to the north-west.

The surrounding seas abound with rocks and reefs ; notable are the Shag Islands and Wakefield Reef, situated respectively a few miles off the central eastern and western coasts of Heard Island.

Description.

Heard Island is almost circular in plan, but is modified by two opposing appendages. The coastline is precipitous ; rock cliffs and the vertical ice fronts of glaciers alternate. These cliffs sweep rapidly upwards to form the mountain mass known as Big Ben Range, which is almost completely snow and ice covered. Several minor peaks are located here, e.g. Fremantle Peak (7800 ft.) and Campbell Peak (7923 ft.), whilst the culminating peak is Mt. Mawson (9005 ft.). This cone-shaped peak has a crater at the top and rises about 1000 ft. above the semi-plateau-like top of Big Ben Range.

Cape Laurens is an imposing mass of small dimensions joined to the island by a narrow tract of low land. The coast is composed of rock cliffs varying from 100 ft. to 1000 ft. in height. The northernmost extremity is Red Island, an extinct volcano (309 ft.), joined through a spit-like junction, thus forming a tied island. The summits of Cape Laurens are snow fields and ice sheets, and the spine-like Mt. Anzac is the highest point (2347 ft.). Lesser peaks are Mt. Dixon (2316 ft.) and Mt. Olsen (2080 ft.).

The south-eastern end of the island is a spit-like structure about five miles long, which swings away seaward after the manner of a tail. This area is low lying and contains a shallow lake.

The coastline of Heard Island shows very little relief, consequently bays and inlets are poorly developed. Atlas Cove is the best and is a fjord-like structure. Corinthian Bay is a large semi-circular bay, as is also South West Bay. Beaches occur ; notable are Fairchild Beach and Long Beach, the low land at Atlas Cove, and the boulder beaches of Spit Point.

The island is of volcanic origin and the grandeur and ruggedness are due to the height and mass of Big Ben Range and Mt. Mawson.

The map reproduced here (Fig. 1) is after that produced by the Expedition during 1948.

GLACIOLOGY.

Snow Line.

Fully ninety per cent. of the area of Heard Island is covered with ice and snow throughout the year.

The snow line varies according to the season. In December, 1947, it was at 1000 ft., and remained stationary until the end of April, 1948, when it commenced to descend. By the 1st July, 1948, it had reached sea-level, where it remained until 1st September. At this stage it commenced to retreat and was at approximately 200 ft. at the end of that month. In the middle of November the snow line was at 500 ft., from which it retreated to 1000 ft., reaching this level at the end of the first week in December, 1948.

There was little difference in the level between northerly and southerly aspects.

Glaciers.

Glaciers on Heard Island may be discussed under two headings : those situated on Cape Laurens and those on the island proper.

Those situated on Cape Laurens are small in size, due to the small area and low altitude of the collecting grounds. Mt. Dixon is covered by a continuous ice sheet, which descends to approximately 600 ft. Between Mt. Dixon and

Anzac Peak two glaciers rise, one flowing north, the other south.   These descend to approximately 500 ft., where they ablate amongst small piles of moraine.
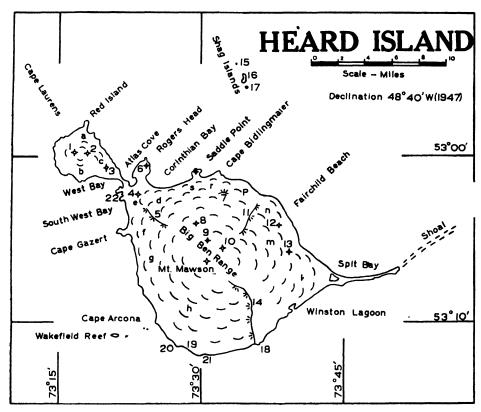
Fig. 1.—Key to Map of Heard Island.   Minor Geographical Features.

Glaciers.

1. Mt. Dixon   ..   ..   2316 ft.
2. Anzac Peak ..   ..   2347 ft.
3. Mt. Olsen   ..   ..   2080 ft.
4. Mt. Drygalski   ..   690 ft.
5. North-West Cornice
6. Corinthian Head   ..   592 ft.
7. Melbourne Bluff   ..   1265 ft.
8. Little Matterhorn   ..   4856 ft.
9. Fremantle Peak   ..   7800 ft.
10. Campbell Peak   ..   7923 ft.
11. North Barrier
12. Round Hill   ..   ..   1252 ft.
13. Scarlet Hill ..   ..   1346 ft.
14. South Barrier
15. Sail Rock   ..   ..   56 ft.
16. Shag Island ..   ..   301 ft.
17. Drury Rock   ..   122 ft.
18. Cape Lambeth   ..   700 ft.
19. Long Beach
20. Cape Labuan   ..   130 ft.
21. Cape Lavett
22. Cave Bay

a. Unnamed.
b.   ,,
c. Jacka Glacier.
d. Baudissin Glacier.
e. Schmidt Glacier.
f. Vahsel Glacier.
g. Abbotsmith Glacier.
h. Gotley Glacier.
k. Unnamed.
m.   ,,
n. Compton Glacier.
p. Unnamed.
r.   ,,
s. Challenger Glacier.

The eastern wall of these glaciers is an almost vertical cliff, which is a structural geological feature, a fault scarp.

Between Mt. Olsen and Anzac Peak and flowing east towards Atlas Cove is the Jacka Glacier. This is the largest glacier of Cape Laurens and was undoubtedly a hanging glacier to the former and now non-existent glacier flowing northwards down Atlas Cove. This older glacier appears to have been of the valley type with Cape Laurens forming the western wall. At the top of the cliffs here is a typical alb formation, indicating the upper limit of the glacier. As the course of this old glacier is intersected by a relatively recent geological fault of large throw, it is evident that the retreat was caused by the lowering of the collecting grounds.

The glaciers situated on the island proper rise from the heights of Big Ben Range. Many reach the sea, but occasionally the front is land-based. Whilst all of them show the effect of plucking action of ice on the underlying rock, generally walls and sides of rock are wanting. It is frequently difficult to determine the boundaries. Often these are low discontinuous mounds of highly crevassed ice. The glaciers lack well defined cirques.

The course of the typical glacier is interesting. Rising on Big Ben Range, the ice flows over the rim of the plateau through areas of intense crevassing. The ice then enters a structure resembling an avalanch-shute, the top of which is marked by a rock cliff normal to the course. Re-formation takes place between two lateral rock walls which are thickly encrusted with ice. Pinnacles and aiguilles are common on these walls. The surface of the glacier now becomes convex in profile and the lateral walls become insignificant. One glacier may contain several of these amphitheatre-like structures. That these are not cirques is indicated by the fact that the material entering is already blue ice.

The glaciers therefore resemble ice sheets modified by plucking action at certain places. Consequently they are to be considered as belonging to the Spitzbergen type.

Although many glaciers are sea-based, none is actually afloat. It was considered that the ice foot was not far vertically below sea-level.

The total depth of ice is uncertain, but measurements taken on the fronts of glaciers indicate that probably 150 ft. may be the upper limit. For example the front of the Baudissin Glacier was measured at 110 ft. in August, 1948, whilst the front of the Vahsel Glacier was 125 ft. thick in the same month. Although the fronts are thinner than the main masses due to ablation, the observations were taken when ablation was at a minimum.

Retreat of Glaciers.

Recent retreat of glaciers and evidence of loss of ice cover in the Antarctic have been reported by Warner (1945) and Knowles (1945). The former has evidence to show the loss of " several hundred vertical feet " of ice.

An indication of a similar recent diminution on Heard Island is afforded by the terminal and lateral moraines of the Vahsel Glacier. The front of this glacier abuts in part on to Cape Gazert, a small headland of bedded lavas. Overlying these lavas are two terminal moraines, as indicated in Figure 1. The terminal moraine situated immediately at the glacier front has an altitude of approximately 125 ft., whilst a short distance away is an older and more consolidated moraine of altitude 320 ft. approximately. The evidence indicates a loss of at least 200 ft. vertical thickness of ice but little horizontal retreat along the glacial path. The lateral moraine of the same glacier shows a similar diminution, as shown in Fig. 2. The older moraine here has an altitude of 300 ft., which is approximately 220 ft. higher than the more recent moraine.

Ablation of Glaciers.

Dissipation of ice takes place by melting, by the action of the sea, or by avalanching.

Melting takes place through the action of the sun, wind and rain.   These agencies are seldom significant above 1000 ft.   During November, 1948, an ablatograph was maintained on the north slopes of the Baudissin Glacier.   The
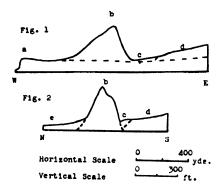
Fig. 2.

Fig. 1 above.   Section at Cape Gazert, indicating retreat of the Vahsel Glacier.
Fig. 2 above.   Section near Erratic Point.   The lateral moraine of the Vahsel Glacier,
indicating retreat.

a. Bedded lavas.	d. Vahsel Glacier.
b. Old moraine.	e. Redistributed·moraine.
c. Active moraine.	

Datum lines are at sea-level.

apparatus was at 125 ft. above sea-level, and the record concerns the ablation of clear blue ice.   In general the ablation was greater during the hours of daylight than during darkness, and rain, however cold, was more effective than sunshine, which in turn was more effective than wind.   The following condensed record illustrates these points.

	Typical Period of Sunshine. Decrease/Hour. Average, Inches.	Typical Period of Light Fairly Constant Rain. Decrease/Hour. Average, Inches.	Typical Period of Wind. Overcast. Decrease/Hour. Average, Inches.
12 p.m. to 3 a.m.	0·00	---	0·02
3 a.m. ,, 6 a.m.	0·00	---	0·00
6 a.m. ,, 9 a.m.	0·03	0·15	0·00
9 a.m. ,, 12 noon	0·05	0·14	0·02
12 noon ,, 3 p.m.	0·12	0·20	0·00
3 p.m. ,, 6 p.m.	0·06	0·06	0·00
6 p.m. ,, 9 p.m.	0·00	0·03	0·00
9 p.m. ,, 12 p.m.	0·00	---	0·00

During the entire month ablation at this station from all causes averaged 0·02 in. per hour approximately.

The melt water finds its way into the ice through crevasses, sinks and crevices, emerging as a torrent through a circular hole at the front of the glacier. In hanging glaciers this water issues as a waterfall, but in the case of sea-based types a discoloured stream enters the sea.   In February, 1948, the glacial stream from the Challenger Glacier was discernible two and a half miles to seaward, whilst in February, 1949, sea water five miles off the south-eastern end

of the island was strongly discoloured. In this case the effect is due to a coalescence of the streams as they are swept eastwards round the flanks of the island by the westerly drift of wind and sea.

The sea is effective in the dissipation of glacial ice. The action is twofold. The pounding of the waves causes undercutting at the foot, resulting in avalanching of the front. Secondly, the deposition of salt spray on the lower level ice causes deterioration of the surface and an opening of cracks and crevasses, which later become lines of weakness along which the avalanches shear off.

Avalanches of this kind vary in size. On the Baudissin Glacier, where the front averaged 100 ft. high, the falls were about 100 yards in length. The ice which falls into the sea is well fragmented, so that large bergs do not result.

Movement of Glaciers.

Observations were carried out on the Baudissin Glacier between the months September to December, 1948. The observation poles were at an altitude of 300 ft. approximately, about half a mile inland. The maximum movement recorded was at the centre, where a movement averaging one foot per day was recorded for the period 11th September to 20th October. In the period 20th October to 8th December this had increased to a daily average of three feet.

Types of Moraines.

Land-based glaciers end in a terminal moraine ; in sea-based types shallow water extends offshore for some distance. Lateral moraines are usually small in size, due to the lack of well-defined walls. The lateral moraine on the north side of the Vahsel Glacier is the largest on the island. It ends in the geographical feature Erratic Point, which contains the largest erratics encountered. Several of these are of the order of 1000 tons. The unusual development of this moraine is due to the high, cliff-like wall, the North West Cornice, which contains the glacier in the lower reaches.

The material deposited ranges from rock flour to boulders of the size mentioned above. Large boulders are rare, the bulk of the material being less than three feet in diameter. Whereas the bulk of material in lateral and medial moraines is angular, the material of the terminal moraines contains a large proportion of rounded and sub-rounded débris. Rounded débris weathers out of solid ice high up on the glacial fronts, as well as issuing with melt water from various tunnels. Scratched and soled pebbles are uncommon, but are more abundant in lateral moraines than in terminal moraines.

Medial moraines are few and small in size ; noteworthy are the two medial moraines of the Compton Glacier. Knob and kettle-structure on a small scale occurs in the moraine of the glacier confronting Saddle Point.

An unusual feature is the large redistributed moraine of Atlas Cove. This has been derived from waste of the Baudissin, Schmidt and Vahsel glaciers, which converge at this point, and possibly in part from the old, now non-existent, glacier flowing down Atlas Cove. The area is flat with a maximum elevation of 60 ft. The débris has been modified by the action of wind and waves and also by slumping, so that it assumes the nature of a plain.

Evidence of bodily shift of these sediments was provided by a stake in the sediments between Corinthian Bay and Mt. Drygalski. This stake moved fifteen feet in eleven months towards Corinthian Bay, thus indicating a spreading by slumping towards deep water. When under the influence of the sea the detrital material becomes subject to westerly drift and is worked round the flanks of the island to the south-east end, where it is deposited in the lee. This has caused the long thin tail-like spit to be built up.

Freezing of Bodies of Water.

Freezing of the sea was noted on 30th July, 1948, and between then and 14th October freezing occurred on eighteen occasions. This was confined to relatively quiet bodies of sea water and took the form of pancakes of ice and slush. The freezing occurred most commonly on clear nights. The solid phase separated at a temperature of 28·6° F., and was fresh. The most severe case of freezing of the sea was noted on 15th September, 1948.

Snow Types.

Snow falls at sea-level throughout the year; however that which falls during summer is quickly dissipated and cold rain is more common. Falls during the winter build up large drifts. An analysis of observations on snow seen to fall about the base camp during the period 1st September to 1st December, 1948, showed that almost 90 per cent. could be classified as either stars, spicules and rods, or frozen rain, the proportions being nearly equal.

Twice during this period snow was observed to accumulate with a preferred orientation. On these occasions the factors were (*a*) the shape of the grains, and (*b*) the influence of the wind. Both times the major axis of the grains was very much longer than the two minor axes, so that the acicular type grains lodged parallel to the surface of the ground and then orientated themselves parallel to the direction of the wind.

SUMMARY.

Heard Island is a small precipitous volcanic island situated within the McDonald Group at 53° south latitude in the Indian Ocean. The climate at sea-level is sub-antarctic. The snow-line is at 1000 ft. during summer but descends to sea-level in winter. During this latter period the sea was observed to freeze. The island is almost completely glaciated and the depth of ice-cover is in excess of 100 ft., although there is evidence to show that this depth was formerly much greater. Descriptions of moraines and glaciers are given and there are also notes on the ablation of ice and the types of snow.

REFERENCES.

Aubert de la Rue, E., 1929. " Un Voyage d'exploration dans les mers Australes. Iles Heard, Archipel de Kerguelen, ile St. Paul." *Rev. de Geogr. Phys. et de Geol. Dynam. Univ. de Paris*, 11, 97-146.

Challenger Expedition, 1885. " Report of the Scientific Results of the Exploring Voyage of H.M.S. *Challenger*, 1873-76." Narrative of the Cruise, 1, Pt. 1, 369.

Drygalski, E. Von, 1908. " Geogr. von Heard Eiland." *Deutsche Sudpolar Exped.*, 1901-3. Bd. 11, Heft 3. Geog. u. Geol. 223-39.

Knowles, P. H., 1945. " Glaciology of Southern Palmer Peninsular Antarctica." Repts. of the U.S. Antarctic Service Expedition, 1939-41. *Proc. Amer. Phil. Soc.* 89 (1), 174.

Mawson, D., 1932. " The B.A.N.Z. Antarctic Research Expedition 1929-31." *Geogr. Jour.*, 80, 105-6.

———.———— 1935. " Some Historical Features of the Discovery of Enderby Land and Kemp Land." *Geogr. Jour.* 86, 526.

Warner, L. A., 1945. " Structure and Petrography of the Southern Edsel Ford Ranges, Antarctica." Repts. of the U.S. Antarctic Service Expedition 1939-41. *Proc. Amer. Phil. Soc.*, 89 (1), 84.

RANK VARIATION IN THE CENTRAL EASTERN COALFIELDS OF NEW SOUTH WALES.

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With Plate III and two text-figures.

INTRODUCTION.

Considerable variation has long been recognised in the nature and properties of coal in the different coalfields situated around the margin of the Permian Coal Basin in Central Eastern New South Wales. It is well known, for example, that coals in the South Coast Field are very friable and " dusty " compared with other fields and that they are characterized by low moisture contents, high carbon contents, low volatile yields, and excellent coking properties. Coals from the Northern, South-western and Western Fields are less friable, contain more moisture and less carbon, give higher volatile yields, and, with some important exceptions in the Newcastle-Swansea area, are more suitable for gas-making and steam-raising than coke production. In the Ulan-Baerami Field, situated between Mudgee and Muswellbrook, the seams are particularly firm, with relatively high moisture contents, low carbon contents, high volatile yields and very poor coking properties.

Such variations in the nature and properties of coal are due largely to rank differences, or different degrees of metamorphic development. Type differences play only a minor part in variations of properties as all the coals concerned are of the same general type. The investigation recorded in this paper was carried out with the object of obtaining quantitative data bearing on regional variation of rank throughout the Upper Coal Measures of the Central Eastern Coal Basin and on the metamorphic history of the area. Results also have some bearing on the relationship between different chemical and physical rank indices.

The coal-bearing strata of the Newcastle stage of the Upper Coal Measures are continuous throughout all the coalfields. The Tomago Measures outcrop only in the Northern Coalfield but the coal is generally similar in rank and type to coal of the Newcastle Measures in the same section of the coalfield, and for the purpose of the present paper coals of the two stages of the Upper Coal Measures are considered together. The Greta or Lower Coal Measures also outcrop on the Northern Coalfield but they contain coal of a somewhat specialised type, which differs from coal of the Upper Coal Measures in nature and condition of original plant material. In view of this and the substantial differences in stratigraphical position, the Greta coal is not included with the Upper Coal Measure coals in considering regional rank variation, but the relation of its rank to other Permian coals is discussed separately. The Permian coals of the Werris Creek-Curlewis-Gunnedah Coalfields are not included in the present work as the coal-measure strata in that area form part of the Great Artesian Basin, and the rank of the coal is not directly related to the tectonic history of the Central Eastern Coal Basin.

I

Vitrain, which is coalified wood and bark, was used for the study of rank variation so as to eliminate, as far as possible, the influence of varying proportions of " banded constituents ". Blocks of coal containing well-developed vitrain bands were obtained from 48 collieries and fresh exposures of coal seams in the different coalfields. In the case of each locality involving the area of a colliery workings, or a fresh exposure of a seam in a railway tunnel or cutting, pure vitrain was separated by hand from at least five or six different bands. Aggregate samples so obtained were analysed to provide average results for vitrain in each locality and to eliminate to some extent variations inherent in the nature of the vitrains. The materials were crushed, sieved and water saturated, then acid washed to remove as much adherent mineral matter as possible. After complete removal of acid by prolonged soaking in water and repeated washing, the samples were used for determination of carbon and hydrogen by ultimate analysis ; volatiles, fixed carbon and ash by proximate analysis ; and maximum inherent moisture by " controlled vaporization of adherent moisture " (Dulhunty, 1947a). Results of the chemical and physical determinations for the vitrains are recorded in Table I.

The ultimate and proximate analyses provide two sets of chemical-rank indices. Values for maximum inherent moisture provide an index of physical rank. The expression " physical rank " is used in relation to progressive changes in the physical state of coal as it matures under natural metamorphism (Dulhunty, 1947b and 1948). It is concerned largely with the degree of physical development of micelle or ultra-fine structure of the coal, and it has been shown that this is closely related to values for maximum inherent moisture (Dulhunty, 1947b ; Hinder, 1949).

RELATIONS BETWEEN DIFFERENT RANK INDICES

Relations between results of proximate and ultimate analyses as chemical rank indices and maximum inherent moisture as a physical rank index were examined by plotting different properties against each other. In Fig. 1 carbon was plotted against fixed carbon for each of the vitrains analysed. The points fall in a relatively wide zone which rises across the diagram from left to right. From the width of the zone it is evident that they are not closely related. Vitrains with any given carbon content may vary in fixed carbon over a range of about 10 per cent. and those of any given yield of fixed carbon may vary in carbon by about 8 per cent. The points fall towards the upper or lower limits of the zone, or the carbon-fixed carbon ratio deviates from the mean, without any apparent reason. The deviation is not related to geographical position or stratigraphical horizons in the coalfields, nor is it related to physical rank of the vitrains, or to the carbon-fixed carbon ratio of the coal seams in which the vitrains occur. It may, however, be related to other factors, such as petrological constitution, which remained to be investigated. It is also possible that deviation of the carbon-fixed carbon ratio may be related to some variable factor in the chemical constitution of the coal substance. In view of this, and the fact that fixed carbon values vary with the conditions of determination, it would seem that carbon content probably represents a more reliable and significant index of chemical rank than fixed carbon. It is evident, however, that fixed carbon may be regarded as a general indication of rank within the limits of variation corresponding to the width of the zone in Fig. 1.

The relations between physical and chemical rank have been studied by plotting values for maximum inherent moisture against carbon of vitrains in all stages of metamorphic development (Dulhunty, 1948). Results showed a zonal relationship with a well-defined maximum at about 68 per cent. carbon and a minimum at about 89 per cent. carbon. The width of the zone, which varies considerably with rank (as illustrated in the above references), is regarded

TABLE I.

Results of Analyses of Vitrain Samples.

Coalfield.	Locality.	Seam.	C.S. No.	Percentage Ash-Free Dry Coal.		Ash Percentage Dry Coal.	M.I.M. Percentage Ash-Free Dry Coal.
				C.	F.C.		
South Coast	Sydney ..	No. 1	30	88·3	77·3	1·1	3·2
	Helensburgh ..	No. 1	312	88·0	76·0	0·9	1·8
	Clifton ..	No. 1	313	88·8	75·4	0·9	1·8
	Austinmer ..	No. 1	314	88·9	73·0	0·8	2·3
	Bulli	No. 1	445	89·7	72·3	1·7	1·9
	Bellambi ..	No. 2	356	89·7	73·6	1·1	2·3
	Corrimal ..	No. 1	394	87·3	73·5	0·6	2·1
	Keiraville ..	No. 1	444	88·3	70·4	3·7	2·0
	Unanderra ..	No. 3	439	88·4	73·5	3·2	1·9
	Unanderra ..	No. 2	352–88	88·1	71·5	0·5	2·5
	Dapto	No. 3	443	88·1	71·4	2·6	2·0
South Western	Berrima ..	No. 3	347–8	84·8	67·8	4·7	4·1
	Nattai ..	No. 3	681	84·9	66·8	2·2	3·0
Western	Katoomba ..	No. 1	671	82·4	67·8	2·9	3·0
	Lithgow ..	No. 7	446	84·6	68·0	2·6	7·4
	Lithgow ..	No. 7	362	83·0	66·9	0·8	5·0
	Lidsdale ..	No. 6	360	85·6	64·7	2·2	7·7
	Cullen Bullen	No. 6	366–7	82·4	63·8	1·2	6·0
	Cullen Bullen	No. 6	430	81·2	63·4	1·4	6·0
	Glen Davis ..	No. 1	667	83·5	67·7	4·2	4·1
	Charbon ..	No. 7	373	83·7	66·5	0·8	8·3
	Kandos ..	No. 7	181	80·8	64·5	2·1	6·4
Ulan-Baerami	Ulan	No. 7	667	78·5	62·0	1·6	9·5
	Wollar ..	No. 6	651 653 656	82·4	63·5	1·6	11·3
	Kerrabee ..	No. 6	666	78·3	65·6	2·5	10·9
	Kerrabee ..	No. 6	673	80·0	66·7	1·9	11·8
	Baerami ..	No. 3	672	79·2	66·5	0·6	9·0

TABLE I.—*Continued.*
Results of Analyses of Vitrain Samples.—Continued.

Coalfield.	Locality.	Seam.	C.S. No.	Percentage Ash-Free Dry Coal.		Ash Percentage Dry Coal.	M.I.M. Percentage Ash-Free Dry Coal.
				C.	F.C.		
Northern	Muswellbrook ..	Tomago Measures	675	85·0	70·4	1·9	4·3
	Liddell ..	Tomago Measures	174	81·0	61·6	3·1	4·0
	Rix Creek ..	Tomago Measures	447–52	81·8	62·6	2·0	4·6
	Rix Creek ..	Tomago Measures	172	80·9	63·6	4·4	6·0
	East Maitland	Tomago Measures	363	79·4	64·4	0·7	4·9
	East Maitland	Tomago Measures	364	81·7	64·7	2·1	4·7
	West Wallsend	Tomago Measures	169	81·3	66·1	1·8	5·6
	Adamstown ..	Victoria Tunnel	353	83·4	62·9	5·1	3·9
	Whitebridge ..	Borehole	377	82·2	64·0	3·0	4·4
	Whitebridge ..	Victoria Tunnel	396	82·3	64·0	2·5	4·6
	Redhead ..	Victoria Tunnel	458	83·7	64·3	3·4	4·0
	Belmont ..	Borehole	404 433	84·7	65·8	0·5	3·9
	Belmont ..	Victoria Tunnel	405 435	82·8	66·1	2·2	4·4
	Belmont ..	Great Northern	459	83·4	63·7	2·4	4·8
	Swansea ..	Wallarah	461	79·8	64·2	5·6	6·1
	Catherine Hill Bay	Wallarah	460	84·05	67·8	1·7	5·8
Greta	Cessnock ..	Greta	310	80·8	62·2	1·6	4·0
	Kearsley ..	Greta	408–9	81·6	62·9	2·2	3·9
	Kearsley ..	Greta	401 403	81·8	65·8	1·3	4·4
	Pelaw Main ..	Greta	390 393	82·6	62·9	1·3	4·0
	Muswellbrook ..	Greta	412 413	80·7	63·8	0·6	8·1

as an indication of the extent to which the two forms of rank may become separated in degree of advancement during metamorphic development. If a point falls towards the lower limits of the zone, between 68 and 89 per cent. carbon, it means that its physical rank is considerably in advance of its chemical rank. Conversely, if a point falls near the top of the zone, between the same limits of carbon, its chemical rank is in advance of its physical rank.

The relationship between chemical and physical rank for vitrains of the Central Eastern Coal Basin is illustrated in Fig. 2. Owing to the limited range in rank of the vitrains concerned (78–90 per cent. carbon), this diagram represents only that portion of the zone where it approaches the minimum at 89 per cent. carbon. It will be noted in Fig. 2 that there is a distinct crowding of points on
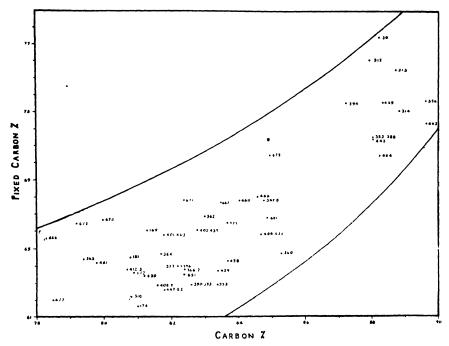
Fig. 1.—Relations between Carbon and Fixed Carbon for Aggregate Vitrain Samples.

the lower side of the zone. From this it may be inferred that vitrains from the majority of localities are considerably more advanced in physical rank than chemical rank. The few vitrains which fall towards the upper side of the zone are all from the western margin of the coal basin in the Western and Ulan-Baerami Coalfields, suggesting that these were the only areas in which conditions of metamorphism were such as to advance chemical rank more than physical rank. These points which fall close to the lower limits of the zone are all from the Maitland-Liddell-Cessnock section of the Northern Coalfield, suggesting the existence of conditions capable of advancing physical rank more than chemical rank. Such results may have an important bearing on prevailing conditions of metamorphism in different parts of the coal basin and on the tectonic history of the coal measures when more is known about the relative influence of various metamorphic factors in the process of coalification.

REGIONAL VARIATION OF CHEMICAL AND PHYSICAL RANK.

In the study of regional variation of physical and chemical rank in the Upper Coal Measures maximum inherent moisture and carbon were used

respectively as indices of the two forms of rank. The area of the Central Eastern Coal Basin and its arbitrary subdivision into coalfields, is shown on the accompanying map (Plate III). Localities from which vitrains were selected for the investigation are indicated by small crosses numbered with the serial numbers of vitrain samples in Table I, which supplies detailed chemical and physical data. The values for carbon and maximum inherent moisture shown on the map represent average results for vitrain in the vicinity of the places where the figures appear. In each the average was obtained for all vitrains in an area extending about halfway to the nearest place where another average is shown. Average results of this kind were placed on the map as the printing of individual results produced too much confusion, and because small local variations in properties tended to obscure the general picture of regional variation. " Isocarbs " or lines indicating distribution of carbon content were drawn on the map at intervals of 2 per cent. from 78 to 90 per cent. carbon. Similar lines
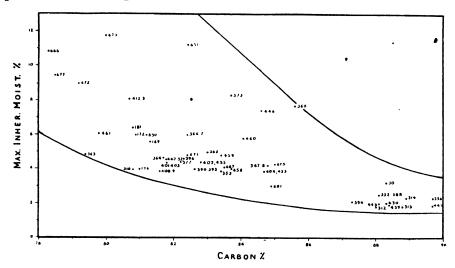
Fig. 2.—Relations between Carbon and Maximum Inherent Moisture for Aggregate Vitrain Samples.

were drawn for maximum inherent moisture at intervals of 1 per cent. from 2 to 11 per cent. These lines have been termed " isomoists " for the purpose of the present paper.

Distribution of chemical rank illustrated by the isocarbs shows a general centre of metamorphism or maximum rank advancement in the vicinity of the South Coast Coalfield. Rank decreases rapidly towards the South-western Coalfield and somewhat less rapidly in the direction of the Northern Coalfield, whilst in a north-westerly direction it decreases very slowly through the centre of the coal basin. Rank also decreases through both the Western and Northern Coalfields towards the Ulan-Baerami Field, where the coals of lowest rank are situated. The centre of high rank on the South Coast is situated towards the southern margin of the coal basin and does not coincide with the general centre of sedimentation or the structural centre of the basin. Beyond the influence of the high rank centre in the south, the isocarbs tend to follow the original shore lines of coal-measure sedimentation. They also appear to be somewhat crowded along the marginal areas leaving a large area in the central region where rank variation is only slight.

Physical rank variation illustrated by the isomoists follows the same general trends as the distribution of chemical rank. A centre of high physical rank with

low moisture values is situated in the vicinity of the South Coast Coalfield and values increase as rank becomes lower through the Western and Northern Coalfields towards the Ulan-Baerami area, where the highest moisture values occur in coals of the lowest rank. As in the case of chemical rank there is a relatively rapid decrease in physical rank, or crowding of isomoists, along the marginal areas of the basin and variation is slight in the central region.

Although the two forms of rank show the same general distribution in relation to the coal basin there are some small but very significant differences in rate of variation. In the Western and Ulan-Baerami Coalfields the isomoists are far more crowded than the isocarbs indicating that physical rank decreases more rapidly than chemical rank. This can be correlated with the conclusion, based on the positions of vitrains in the zonal relationship between moisture and carbon (Fig. 2), that in the Western and Ulan-Baerami Coalfields conditions of metamorphism were such as to advance chemical rank more than physical rank. If chemical rank is more advanced that physical rank then the rate of change in physical rank on passing towards the Ulan-Baerami Field, will be greater than change in chemical rank. This is so as the isomoists are more crowded than the isocarbs in the Ulan-Baerami Coalfield. Similarly it was concluded in discussing Fig. 2 that physical rank was more advanced than chemical rank in parts of the Northern Coalfield, and it is evident trom the map that isocarbs are somewhat more crowded than isomoists in that area. Another example of correlation between rank distribution and the positions of vitrains on the moisture-carbon diagram can be seen in the South-western Coalfield. In this area isocarbs are more crowded than isomoists and the vitrains fall towards the lower side of the zone in Fig. 2.

From the foregoing discussion and results it would seem to follow that features such as relative crowding of isocarbs and isomoists or the different rates at which physical and chemical rank vary from place to place, and the crossing of isocarbs and isomoists must be related to differences in metamorphic conditions or the predominance of different metamorphic factors which have existed in various regions of the coal basin. As stated earlier, when more is known about the relative influence of different metamorphic factors during coalification it is highly probable that much information about the geological history of coal measures will be revealed by relations between the distribution of physical and chemical rank, as illustrated by isocarbs and isomoists in Plate III.

STRATIGRAPHICAL VARIATION IN RANK.

In many coalfields of the world the coal seams exhibit a definite increase in rank with depth from the surface. This is generally attributed to increase in pressure and temperature with depth. In the Central Eastern Coal Basin of New South Wales there is a general tendency for isocarbs and isomoists to follow the original shore lines of deposition along the western and north-eastern sides of the basin where rank increases on passing towards the central regions. This is probably due to increases in depth of cover, but the principal trends in rank variation are not related to depth of burial or thickness of the coal measures. For example, rank decreases progressively from 84 per cent. carbon to 78 per cent. carbon in a northerly direction along the western margin of the basin. The centre of high rank on the South Coast is situated towards the southern margin of the basin and cannot be correlated with either depth of burial or thickness of coal measures. The highest and lowest rank coals occur in the South Coast and Ulan-Baerami Coalfields respectively although depth of burial in each case, and physiographic histories of the two areas, appear to have been much the same.

Vitrain bands occur in the topmost beds of Triassic sandstone near Sydney. The rank of the Triassic vitrains (about 86 per cent. carbon) is almost as high

as that of Permian vitrains (88 per cent. carbon), which occur some 3000 ft. deeper in the same area. Also, the rank of the Triassic vitrain is much higher than the Permian vitrains along the western and north-western sides of the basin. The strata are practically undisturbed by folding or faulting in any of these areas. It is possible that the high carbon contents of the Triassic vitrains near Sydney may be due to coalification in a sandstone environment rather than the general coal-measure environment in which the underlying Permian vitrains were formed. If, however, their high carbon contents resulted from regional metamorphic conditions, which appears likely, then some factors other than depth must have produced the high-rank coals between Sydney and Wollongong and those factors would appear to have operated in post-Triassic time. The large number of igneous sills and dykes injected into the coal measures and underlying marine beds along the South Coast may have elevated the general temperature of the strata sufficiently to produce coals of higher rank than in any other part of the coal basin. In general, however, it appears that rank variation in the Central Eastern Coal Basin is not a simple consequence of depth of burial, and cannot be related to folding or other tectonic disturbances in the coal measures.

REFERENCES.

Dulhunty, J. A., 1947a. THIS JOURNAL, 81, 60.
—.———— 1947b. *Aust. Jour. Sci.*, 9, No. 4, 133.
—.———— 1948. THIS JOURNAL, 82, 265.
Hinder, Nora, 1949. *Ibid.*, 83, 195.

STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART IV. OXIDATION OF IONS OF THE TETRAMMINE PLATINUM II TYPE WITH HYDROGEN PEROXIDE.

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Platinum (IV) compounds of the type $[Pt(NH_3)_4Y_2]X_2$ are, in general, prepared by oxidation of the tetrammine platinum (II) ion, using a source of the group it is desired to introduce as oxidising agent, when the compound of quadrivalent platinum is formed, e.g.,

$$[Pt(NH_3)_4]^{++} + Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{++}$$

When H_2O_2 is used as oxidising agent in aqueous solution the corresponding dihydroxo compound is formed.

$$[Pt(NH_3)_4]^{++} + H_2O_2 \longrightarrow [Pt(NH_3)_4(OH)_2]^{++}$$

Apart from salts of the dihydroxo tetrammine platinum (IV) ion, which are well known, compounds in which the ammonia groups are replaced by other coordinated groups do not appear to have been prepared previously.

In a previous communication it is reported that the attempted oxidation of tetra pyridine platinum II fluoride with hydrogen peroxide was unsuccessful. We have now made further attempts to oxidise the tetrapyridine platinum II ion with hydrogen peroxide. Reaction of the chloride of this ion with aqueous hydrogen peroxide under the same conditions used for oxidation of tetrammine platinum II chloride does not appear to bring about oxidation and tetrapyridine platinum (II) chloride can be recovered from the reaction mixture. An aqueous solution of the perchlorate does not discolour potassium permanganate.

Compounds in which one or more of the pyridine groups in the tetra pyridine platinum (II) ion are replaced by ammonia can be prepared.

Trans dipyridine diammine platinum (II) chloride reacts with hydrogen peroxide, oxidation taking place to yield the corresponding dihydroxo platinum IV chloride, from which other salts can be prepared by double decomposition in aqueous solution. These are generally colourless, crystalline compounds, moderately soluble in cold water and readily soluble in hot water. With potassium chloroplatinate (II) and chloroplatinic (IV) acid the ion yields sparingly soluble coloured compounds, the compound obtained from the chloroplatinate (II) being of uncertain structure, due to the possibility of simultaneous oxidation-reduction occurring. It has thus been shown that analogous reactions with hydrogen peroxide and the tetrammine platinum (II) ion occur when two of the ammonia groups are replaced by pyridine molecules. The $-OH$ groups are most likely in the trans or $1:6$ positions.

In the postulate of essential electrical neutrality of atoms (Pauling, 1948) the charge on a complex ion is considered to be localised mainly on the peripheral hydrogen atoms of hexaquo or hexammine ions. If the postulate is extended to planar tetrammine ions of platinum (II) we can consider the greater portion of the charge of $2+$ located on the twelve hydrogen atoms in $[Pt(NH_3)_4]^{++}$

leaving the platinum atom with only fractional charge. With the tetrapyridine platinum (II) ion such a charge distribution is less favoured resulting in a numerically greater positive charge on the platinum atom. On the basis of this postulate it would appear that these structural differences are somehow intrinsically associated with the lack of reaction of the $[PtPy_4]^{++}$ with H_2O_2. Replacement of two pyridine molecules by ammonia sufficiently alters the structure as to permit reaction with H_2O_2.

The above example of the influence of attached pyridine groups on the reactions of a complex ion is probably one of a general type. Thus it has been shown (Friend and Mellor, 1947) that when trans-dichlorotetrapyridine cobalt (III) chloride reacts with pyridine, reduction occurs and tetrapyridine cobalt (II) chloride is formed, chlorine being liberated during the reaction. This suggests that a complex cobalt ion with more than four attached pyridine groups is incompatible with the increased charge required on the ion.

Evidence that, when the coordination number of a metal is satisfied by pyridine molecules, the lower oxidation state is favoured has been demonstrated by Dwyer and Nyholm (1942). These authors succeeded in preparing hexapyridine rhodium (II) compounds, halogeno pentapyridine rhodium (II) and other compounds in the pyridine rhodium (II) series. Attempts to prepare similar compounds of rhodium (II) containing ammonia and ethylenediamine were unsuccessful, only rhodium (III) compounds being obtained (private communication from Dr. F. P. J. Dwyer).

EXPERIMENTAL.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum IV Chloride 1·5 Hydrate.

Trans- $[Pt(NH_3)_2(C_5H_5N)_2]Cl_2.H_2O$ (Drew, Pinkard, Wardlaw and Cox, 1932) (1·0 g.) was treated with 30% H_2O_2 (6 ml.); oxygen was evolved and the temperature of the solution rose to about 35° C. On standing crystals were deposited in well formed cubes with some tetragonal forms present. Further crystallisation was induced by the addition of acetone. Yield 1·1 g. Recrystallised from hot water, yield 0·9 g., in small colourless tetragonal crystals of the 1·5 hydrate moderately soluble in water (about 6–7 g./100 g. at 5° C.). Over P_2O_5 the water of crystallisation was lost and regained on exposure to air.

Found (on air dry material) : Pt, 37·6% ; Cl, 13·8%.

H_2O, 4·8, 5·6. (Lost *in vacuo* over P_2O_5.)

$[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]Cl_2.1·5 H_2O$ requires Pt, 37·6% ; Cl, 13·7% ; H_2O, 5·2%.

1 : 6 Dihydroxo–2 : 4 dipyridine diammine Platinum IV Bromide 2–Hydrate.

The corresponding chloride, recrystallised from water (1·0 g.) was dissolved in minimum quantity of hot water (5 ml.) and 0·7 g. of potassium bromide added. The clear solution was cooled in ice water, when the less soluble bromide crystallised. Yield 1·0 g. Recrystallised from hot water (7·5 ml.) as small colourless tetragonal crystals with (100) faces. The 2-hydrate obtained was only moderately soluble in cold water (about 2·8 g. per 100 g. water at 5–10° C.). Over P_2O_5, 2 molecules of H_2O were lost but are taken up again on exposure to air.

Found (on air dry material) : Pt, 31·7% ; Br, 26·1% ; H_2O, 5·6%. (Loss *in vacuo* over P_2O_5.)

$[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]Br_2.2H_2O$ requires : Pt, 31·6% ; Br, 25·9% ; H_2O, 5·8%.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum (IV) Iodide 0·5 Hydrate.

Prepared from the corresponding chloride and potassium iodide in same manner as described for the bromide. 0·8 g. of the chloride yielded 0·7 g. of the iodide, recrystallised from water. The iodide was only sparingly soluble in water (about 0·5 g./100 g. H_2O at 5° C.), moderately soluble in hot water, from which it crystallised on cooling in colourless crystals of the 0·5 hydrate with tetragonal form showing (100) faces. The water of crystallisation was lost over P_2O_5 and regained on exposure to air.

Found (on air dry material) : Pt, 28·5% ; I, 37·1% ; H₂O, 1·2%. (Loss *in vacuo* over P₂O₅.)

$[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]I_2.0\cdot 5H_2O$ requires : Pt, 28·5% ; I, 37·2% ; H₂O, 1·3%.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum (IV) Nitrate 1–Hydrate.

In an analogous manner to the preparation of the bromide and iodide, 1·0 g. of the chloride with ammonium nitrate yielded 0·6 g. of the nitrate 1-hydrate, recrystallised from water. It was sparingly soluble in water (about 3·8 g. in 100 g. at 5° C.), readily soluble in hot water, from which it crystallised in colourless tetragonal prisms. Water of crystallisation was lost on drying over P₂O₅ and regained on exposure to air. When heated the compound decrepitated.

Found (on air dry material) : Pt, 34·4% ; H₂O, 3·1%. (Loss *in vacuo* over P₂O₅.)

$[Pt(NH_3)_2(C_5H_5N_2)_2(OH)_2](NO_3)_2.H_2O$ requires : Pt, 34·6% ; H₂O, 3·2%.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum (IV) Perchlorate.

As before from the corresponding chloride and perchloric acid, 1·0 g. of the chloride yielded 0·6 g. of the perchlorate recrystallised from hot water. The perchlorate was only moderately soluble in hot water and sparingly soluble in cold water (about 0·5 g./100 g. H₂O at 5° C.), from which it crystallised as colourless monoclinic needles and prisms. The anhydrous crystals were not deliquescent.

Found : Pt, 31·4%.

$[Pt(NH_3)_2(C_5H_5N)_2(OH)_2](ClO_4)_2$ requires : Pt, 31·4%.

Reaction of $[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]^{++}$ with $(PtCl_4)^=$ and $[PtCl_6]^=$.

$[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]Cl_2.1\cdot 5H_2O$ (0·49 g.) in a few ml. of water added to K₂PtCl₄ (0·4 g.) dissolved in the minimum quantity of water, gave an instantaneous precipitate which consisted of small thin, pink coloured plates, resembling graphite in form.

Yield : 0·6 g.

Found : Pt, 51·1%.

$Pt(NH_3)_2(C_5H_5N)_2(OH)_2PtCl_4$ requires : Pt, 51·46%.

Similarly a solution of $[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]Cl_2$ in water with a solution of H₂PtCl₆ yielded an insoluble chloroplatinate (IV), in thin bright orange needles, sparingly soluble in hot water, moderately soluble in hot concentrated hydrochloric from which the chloride crystallises on cooling.

Found : Pt, 47·0%.

$[Pt(NH_3)_2(C_5H_5N)_2(OH)_2]PtCl_6$ requires : Pt, 47·0%.

Trans-dipyridine diammine Platinum (II) Bromide 1–Hydrate.

Trans $[Pt(C_5H_5N)_2(NH_3)_2]Cl_2.H_2O$ (Drew, Pinkard, Wardlaw and Cox, 1932) (0·7 g.) was dissolved in hot water (4 ml.) and 0·6 g. potassium bromide added. The bromide was precipitated immediately ; yield 0·7 g. Recrystallised from hot water (6 ml.) as colourless tetragonal needles and prisms. The hydrate obtained was only moderately soluble in cold water (2·7 g. per 100 g. water at 15° C.). Over P₂O₅ one molecule of H₂O is lost.

Found (on air dry material) : Pt, 34·5% ; Br, 28·6% ; H₂O, 2·94%.

$[Pt(NH_3)_2(C_5H_5N)_2]Br_2.H_2O$ requires : Pt, 34·5% ; Br, 28·3% ; H₂O, 3·18%.

Trans-dipyridine diammine Platinum II Iodide.

Prepared from the corresponding chloride and potassium iodide in the same manner as used for the bromide. 0·4 g. chloride yielded 0·33 g. of iodide, recrystallized from water. The iodide was sparingly soluble in water (0·5 g. per 100 g. of water at 15° C.), moderately soluble in hot water (about 4 g. per 100 g. water at 100° C.). It crystallized as anhydrous colourless tetragonal prisms.

Found : Pt, 30·4% ; I, 39·2%.

$[Pt(C_5H_5N)_2(NH_3)_2]I_2$ requires : Pt, 30·4% ; I, 39·6%.

Trans-dipyridine diammine Platinum II Nitrate.

The nitrate was prepared from the chloride in a similar manner to the bromide and iodide. 0·6 g. of the chloride treated with ammonium nitrated yielded 0·6 g. of the nitrate, which on recrystallization from water yielded 0·22 g. The nitrate was only moderately soluble in cold water (about 6 g. per 100 g. water at 15° C.) but very soluble in hot water (about 40–50 g. per 100 g. at 100° C.), from which it crystallized in anhydrous colourless tetragonal needles and prisms.

Found : Pt, 38·3%.

$[Pt(NH_3)_2(C_5H_5N)_2](NO_3)_2$ requires : Pt, 38·2%.

Trans-dipyridine diammine Platinum II Perchlorate.

This was prepared by the addition of perchloric acid in a solution of the corresponding chloride. 0·8 g. of the chloride yielded 0·57 g. recrystallized from water. The perchlorate was only moderately soluble in hot water (about 6 g. per 100 g. water at 100° C.) and sparingly soluble (about 0·4 g. per 100 g. at 15° C.) in cold water, from which it crystallized as colourless monoclinic needles. The anhydrous crystals were not deliquescent.

Found : Pt, 33·1%.

$[Pt(NH_3)_2(C_5H_5N)_2](ClO_4)_2$ requires : Pt, 33·2%.

Trans-dipyridine diammine Platinum II Chloroplatinate (IV).

A solution of $[Pt(NH_3)_2(C_5H_5N)_2]Cl_2$ in water treated with a solution of H_2PtCl_6 yielded an insoluble chloroplatinate (IV). The product consisted of orange cubes, similar in shape to fluorite. It was found to be insoluble in cold water, very sparingly soluble in hot water, and moderately soluble in hot concentrated hydrochloric acid, from which the chloride crystallizes on cooling.

Found : Pt, 49·0%.

$[Pt(NH_3)_2(C_5H_5N)_2]PtCl_6$ requires : Pt, 49·0%.

SUMMARY.

The preparation of some compounds of the 1 : 6 dihydroxo 2 : 4 dipyridine diammine platinum (IV) ion has been described. The compounds were colourless crystalline compounds only moderately soluble in water. Coloured, insoluble, crystalline compounds were formed when the ion reacted with the chloro-platinate (II) and chloroplatinate (IV) ions. Attempted oxidation of the tetrapyridine platinum (II) ion with hydrogen peroxide, under similar conditions was unsuccessful.

ACKNOWLEDGEMENT.

REFERENCES.

Drew, Pinkard, Wardlaw and Cox, 1932. *J.C.S.*, 1004.
Dwyer, F. P. J., and Nyholm, R. S., 1942. THIS JOURNAL, **76**, 275.
Friend, J. A., and Mellor, D. P., 1947. THIS JOURNAL, **81**, 154.
Pauling, L., 1948. *J.C.S.*, 1461.

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COORDINATION COMPOUNDS OF COPPER.

PART II. COMPOUNDS DERIVED FROM COPPER (I) IODIDE.

By C. M. HARRIS.

Copper (I) halides readily dissolve in boiling concentrated solutions of the corresponding alkali or ammonium halides to form complex halogeno-cuprates (I). Recently the author employed this reaction (Harris, 1948) to isolate tetrammine and bis-ethylenediamine copper (II) dihalogeno-cuprates (I) of the general formula $[Cu^{II}(A)_4][Cu^{I}X_2]_2$ ($A=NH_3$; $2A=C_2H_4(NH_2)_2$ and $X=Br$ and I). With the chloro-complexes the ammonia compound was obtained as the monohydrate $[Cu^{II}(A)_4][Cu^{I}Cl_2]_2.H_2O$ and the ethylenediamine compound possessed the formula $[Cu^{II}(C_2H_4(NH_2)_2)_2]Cu^{I}_3Cl_5$.

It has since been found that copper (I) iodide dissolves in a boiling concentrated solution of alkali or ammonium bromide forming a colourless solution presumably containing the bromo-iodo-cuprate (I) ion.

$$CuI + Br^- \underset{\text{dilution}}{\overset{\text{aqueous } Br^-}{\rightleftharpoons}} [CuIBr]^-$$

Dilution decomposes the complex ion causing copper (I) iodide to be precipitated. That this solution does contain such an ion and is not merely a mixture of the dibromo- and diiodo-cuprate (I) ions is supported by its reactions with ammonia and ethylenediamine described later.

Addition of a solution containing the bromo-iodo-cuprate (I) ion to a solution containing tetrammine copper (II) or bis-ethylenediamine copper (II) ions yields, on cooling, black tetrammine copper (II) bromo-iodo-cuprate (I) $[Cu^{II}(NH_3)_4][Cu^{I}IBr]_2$ (I) and purple bis-ethylenediamine copper (II) bromo-iodo-cuprate (I) $[Cu^{II}(C_2H_4(NH_2)_2)_2][Cu^{I}IBr]_2$ (II) respectively.

Water, particularly on heating, decomposes these compounds, forming a deep blue and

$$[Cu^{II}(A)_4][Cu^{I}IBr]_2 \xrightarrow{\text{water}} [Cu^{II}(A)_4]^{++} + 2Br^- + 2Cu^{I}I$$
$$\downarrow$$

purple solution of tetrammine and bis-ethylenediamine copper (II) bromide respectively and a white precipitate of copper (I) iodide. Addition of acid decomposes the tetrammine ion as well according to the reaction

$$[Cu^{II}(A)_4][Cu^{I}IBr]_2 + 4H^+ \rightarrow Cu^{++} + 2Br^- + 4AH^+ + 2CuI$$
$$\downarrow$$

providing a means of determining the copper (II) ion in the presence of copper (I) since the addition of iodide ions liberates iodine equivalent to the copper (II).

Treatment of compound II with boiling concentrated potassium iodide solution causes it to dissolve and, on cooling, brown prisms of bis-ethylenediamine copper (II) diiodo-cuprate (I) (Harris, *loc. cit.*) are deposited.

Compounds I and II cannot be a physical mixture of the corresponding dibromo- and diiodo-complexes since the diiodo-complexes liberate free iodine (Harris, *loc. cit.*) on treatment with acid and these compounds do not. However, the structures of compounds I and II in the solid state need not necessarily contain discrete [CuIBr]⁻ ions. They could contain both [CuBr₂]⁻ and [CuI₂]⁻ ions.

The reaction of the bromo-iodo-cuprate (I) solution with a limited amount of ammonium hydroxide yielded, on cooling, an amminated copper (I) iodide derivative, $(CuI)_2.NH_3$ (III), as white plates. On reacting a solution containing the diiodo-cuprate (I) ion in a similar manner with ammonium hydroxide an entirely different compound, $CuI.NH_3$ (IV), was obtained as yellow prisms. This reaction supports the postulation of the bromo-iodo-cuprate (I) ion in solution indicating that such a solution is not merely a mixture of [CuI₂]⁻ and [CuBr₂]⁻ ions since if this was the case it should yield the same copper (I) iodide derivative with ammonia as a solution containing only [CuI₂]⁻ ions.

Ethylenediamine fails to react with the bromo-iodo-cuprate (I) solution to yield a copper (I) iodide derivative. On shaking the mixture in the presence of air, oxidation takes place and purple prisms of compound II are deposited. The diiodo-cuprate (I) solution reacts immediately with ethylenediamine to deposit a cream microcrystalline compound, $(CuI)_2.C_2H_4(NH_2)_2$ (V). The filtrate deposited brown prisms of a compound which was most likely bis-ethylenediamine copper (II) diiodo-cuprate (I) resulting from oxidation of copper (I).

The structure of compound III is unknown. Silberrad (1905) reported the preparation of a green compound $Cu_2I_2.NH_3.4H_2O$. Since the preparation was performed in the presence of air in a strongly ammoniacal solution and the water was determined by difference it is quite possible that this compound was an oxidised copper (I) derivative in keeping with its colour.

Compound IV can be formulated as either the monomer $[H_3N \rightarrow CuI]°$, the dimer $[Cu^I(NH_3)_2][Cu^II_2]$, or the tetramer $[H_3N \rightarrow CuI]_4°$. The last structure is similar to the triethyl arsine derivative $[Et_3As \rightarrow CuI]_4°$, whose structure was established by Mann, Purdie and Wells (1936) to consist of a central tetrahedron of copper atoms surrounded by tetrahedral groups of iodine atoms and triethyl arsine molecules. This structure would seem the most likely.

A number of alternative structures are possible for compound V also. It may be formulated as the complex copper (I) cuprate (I), $[Cu^I(C_2H_4(NH_2)_2][Cu^II_2]$. This, however, seems unlikely, since apart from a lack of symmetry the $[Cu^I(C_2H_4(NH_2)_2)]^+$ ion would involve considerable strain in the carbon-nitrogen bonds if it was to possess the linear configuration which is associated with two covalent copper (I) complexes (Wells, 1945). This view is supported by the fact that no compounds containing the ethylenediamine copper (I) ion · are known. Compound V can be satisfactorily formulated with a tetrahedral structure similar to the arsine derivative mentioned previously save that the intramolecular bridging that would be required of ethylenediamine for the existence of discrete tetrahedral molecules in the structure is unlikely from a consideration of bond lengths and angles. An infinite three-dimensional structure, however, would be possible with intermolecular bridging of the tetrahedral units by means of the ethylenediamine.

Compounds corresponding to III and IV have previously been postulated by Biltz and Stollenwerk (1921). They investigated tensimetrically the formation of ammoniates with copper (I) halides and in the case of the iodide obtained evidence for the existence of the ammoniates $CuI.nNH_3$ where $n=0.5, 1, 2$ and 3.

During the course of this work an attempt was made to form the diammine (ethylenediamine) copper (II) ion, $[Cu(NH_3)_2(C_2H_4(NH_2)_2)]^{++}$, in solution and isolate it as its diiodo-cuprate (I) derivative. This was not realised and on reacting one mole of a copper (II) salt with one mole of ethylenediamine and a limited excess of ammonium hydroxide followed by metathesis with a potassium iodo-cuprate (I) solution an earth green mixture of tetrammine and bis-ethylene-diamine copper (II) diiodo-cuprates (I) was obtained. The tetrammine compound in the mixture was decomposed to copper (I) iodide by heating the mixture at 100° C. to constant weight. From the loss in weight was calculated the percentage of tetrammine compound present. The residue was treated with concentrated potassium iodide solution to remove copper (I) iodide and the bis-ethylenediamine compound that remained was filtered off and identified.

Compounds I–V inclusive reduce silver nitrate solution to the metal instantly in the cold due to the copper (I) present in their molecules and also give a simultaneous precipitate of silver halide. They are insoluble in the usual organic solvents and unstable to water.

Copper (I) iodide also dissolves to a small extent in boiling concentrated ammonium and alkali chloride solutions presumably forming the chloro-iodo-cuprate (I) ion. Attempts to isolate this ion as its bis-ethylenediamine copper (II) derivative were unsuccessful due to the large amounts of ammonium or alkali chloride that crystallised out on cooling the reaction mixture.

EXPERIMENTAL.

(1) *Tetrammine Copper (II) Bromo-iodo-cuprate (I).*

To diammine copper (II) acetate (1·6 g., 0·0074 g. mole (Horn, 1908)) dissolved in a solution of ammonium hydroxide (1·3 ml. of 15 N) in water (25 ml.) was added acetic acid (0·3 ml. of 17 N). After the addition of ammonium bromide (5·0 g.) the solution was heated to 80–85° C. A boiling solution of copper (I) iodide (2·8 g., 0·015 g. mole) and ammonium bromide (30 g.) in water (35 ml.) was added in a thin stream with constant stirring and the stirring continued while the solution was cooled to 25° C. After immediate filtration the black microcrystals were washed with 90% alcohol, followed by dry ether. The filtration and washing must be as rapid as possible to avoid oxidation. Yield 2·4 g. (42%).

Found : Cu (total), 28·2 : Cu^{++}, 9·31 ; NH$_3$, 10·1%. 0·497 and 0·502 g. complex gave 0·623 and 0·631 g. of AgBr+AgI.

$[Cu^{II}(NH_3)_4][Cu^IIBr]_3$ requires Cu (total), 28·36 : Cu^{++}, 9·45 ; NH$_3$, 10·13%. 0·497 and 0·502 g. complex give 0·625 and 0·631 g. of AgBr+AgI.

The compound is readily oxidised in the presence of moist air, assuming a greenish colour. Water decomposes it instantly in the cold, according to the reaction given previously. It is unaffected by alcohol, acetone and the usual organic solvents. A cold solution of silver nitrate is instantly reduced by the compound to metallic silver with simultaneous precipitation of silver halides.

(II) *Bis-ethylenediamine Copper (II) Bromo-iodo-cuprate (I).*

To a solution of bis-ethylene diamine copper (II) bromide monohydrate (2·5 g., 0·0069 g. mole (Johnson and Bryant, 1934)) dissolved in water (30 ml.) was added ammonium bromide (5·0 g.), and the solution was heated to 85° C. A boiling solution of copper (I) iodide (2·6 g., 0·015 g. mole) and ammonium bromide (30 g.) in water (35 ml.) was added with constant stirring and the stirring continued while the solution was cooled to 25° C. After filtration the compound was washed with methyl alcohol followed by dry ether. Yield 4·6 g. (92%).

Found : Cu (total), 26·4 ; Cu^{++}, 8·73%. 0·496 g. complex gave 0·474 g. AgBr+AgI.

$[Cu^{II}(C_2H_4(NH_2)_2)_2][Cu^IIBr]_3$ requires Cu (total), 26·3 ; Cu^{++}, 8·77%. 0·496 g. complex gives 0·479 g. AgBr+AgI.

The compound crystallises as purple prisms stable in air. Water decomposes the compound more slowly than the corresponding tetrammine but completely on boiling in accordance with the equation given previously. It reduces silver nitrate solution instantly in the cold to silver with simultaneous precipitation of silver halides. Dilute acetic and sulphuric acid decomposes the compound, according to the equation given previously to copper (I) iodide. (Found : Cu, 66·0 ; calculated : Cu, 66·6%.) The compound dissolves in boiling 50% potassium iodide solution, from which brown prisms of bis-ethylenediamine copper (II) diiodo-cuprate (I) (loc. cit.) is deposited on cooling. (Found : Cu (total), 23·4 ; calculated : Cu (total), 23·3%.) The compound is unaffected by alcohol, acetone and the usual organic solvents.

(III) Monammine Bis-(Copper (I) Iodide).

To copper (I) iodide (2·0 g.) dissolved in a boiling solution of potassium bromide (35 g.) in water (50 ml.) and cooled to 85° C. was added ammonium hydroxide (0·70 ml. of 15 N) with vigorous stirring. The stirring was continued while the solution was rapidly cooled to 25° C. After immediate filtration the compound was washed with 90% alcohol followed by dry ether. The filtration and washing must be as rapid as possible to avoid oxidation. The ether was removed under vacuum and the compound sealed from the atmosphere. Yield 0·8 g. (38%).

Found : Cu, 31·4 ; NH_3, 4·4 ; I, 63·8%. $(Cu^II)_2.NH_3$ requires Cu, 31·9 ; NH_3, 4·3 ; I, 63·8%.

The compound crystallises as lustrous pearly plates and is readily oxidised in the atmosphere assuming a green colour. It is decomposed immediately in the cold by water, with the appearance of the blue tetrammine copper (II) colour due to oxidation. A cold solution of silver nitrate is instantly reduced by the compound to metallic silver, with simultaneous precipitation of silver iodide. On heating at 100° C. to constant weight the compound (0·202 g.) loses its ammonia, and copper (I) iodide (0·192 g.) (calc. 0·193 g.) remains. It is insoluble in organic solvents.

(IV) Monammine Copper (I) Iodide.

To copper (I) iodide (7·5 g.) dissolved in a boiling solution of potassium iodide (45 g.) in water (30 ml.) and cooled to 75° C. was added ammonium hydroxide (2·5 ml. of 15 N) with vigorous stirring. The stirring was continued while the solution was rapidly cooled to 25° C. After immediate filtration the compound was washed with methyl alcohol followed by dry ether. The ether was removed and the compound sealed from the atmosphere. Yield 5·0 g. (61%).

Found : Cu, 30·3 ; NH_3, 8·2 ; I, 61·3%.

$Cu^II.NH_3$ requires Cu, 30·6 ; NH_3, 8·2 ; I, 61·2%.

The compound is decomposed by water similarly to the previous compound and gives the same reaction with silver nitrate. It crystallises as yellow prisms, readily oxidised by the atmosphere, when it assumes a green colour.

(V) Ethylenediamine Bis-(Copper(I) Iodide).

To copper (I) iodide (2·9 g., 0·015 g. mole) dissolved in a boiling solution of potassium iodide (22 g.) in water (15 ml.) and cooled to 55° C. was added a solution of ethylenediamine (0·40 ml. of anhydrous, 0·006 g. mole) and potassium iodide (5·0 g.) in water (5 ml.) at 55° C. with stirring. After immediate filtration the compound was washed with methyl alcohol followed by dry ether. Yield 2·6 g. (98%).

Found : Cu, 28·7 ; I, 57·6%.

$(Cu^II)_2.C_2H_4(NH_2)_2$ requires Cu, 28·8 ; I, 57·5%.

The compound is insoluble in organic solvents and is stable in air. It crystallises as cream micro-prisms and reduces silver nitrate in the cold to metallic silver with simultaneous precipitation of silver iodide. It is insoluble in cold water but decomposed readily on warming, oxidation to bis-ethylenediamine copper (II) iodide taking place (see Morgan and Burstal, 1926). The filtrate from the above preparation deposited a small amount of brown prisms which were probably bis-ethylenediamine copper (II) diiodo-cuprate (I), resulting from partial oxidation of some of the copper (I).

Reaction of Ethylenediamine with a Solution of the Bromo-iodo-cuprate (I) Ion.

To copper (I) iodide (1·0 g.) dissolved in a boiling solution of ammonium bromide (20.g.) in water (20 ml.) and cooled to 60° C. was added a solution of ethylenediamine (0·15 ml. of anhydrous) in water (5 ml.) containing ammonium bromide (5·0 g.) at 55° C. No precipitate appeared on cooling to 30° C. but on shaking for 10–15 minutes purple prisms of compound II were deposited. Yield 0·5 g.

Found : Cu (total), 26·4.

Calculated : 26·3%.

Attempted Preparation of Diammine (Ethylenediamine) Copper (II) Diiodo-cuprate (I).

To a solution of anhydrous copper (II) chloride (0·85 g., 0·0063 g. mole) in water (15 ml.) was added ethylenediamine (0·62 ml. of 69%, 0·0071 g. mole) followed by ammonium hydroxide (1·0 ml. of 15N). After the addition of potassium iodide (2·0 g.) the stirred solution was heated. to 75° C. and to it was added in a fine stream a boiling solution of copper (I) iodide (2·4 g., 0·013 g. mole) and potassium iodide (15·0 g.) in water (10 ml.). The stirring was continued and the solution cooled to 25° C. After filtration the compound was washed with 90% alcohol followed by ether. Yield 4·4 g.

Found : Cu, 23·8%.

Calculated for a 1 : 2 mixture of $[Cu^{II}(NH_3)_4][Cu^{I}I_2]_2$ and $[Cu^{II}(C_2H_4(NH_2)_2)_2][Cu^{I}I_2]_2$: Cu, 23·8%.

The mixture, which was micro-crystalline, possessed an earthy colour with a green reflex. Brown and dark green crystals could be distinguished under the microscope. The mixture (0·511 g.) was heated to 100° C. to constant weight (0·468 g.). From the loss in weight (0·043 g.) the amount of tetrammine copper (II) diiodo cuprate (I) (0·173 g.) present in the mixture was calculated.

The residue was boiled with 50% potassium iodide solution (10 ml.) and on cooling to 30–40° C. the brown bis-ethylenediamine copper (II) diiodo-cuprate (I) was filtered off and washed with 50% potassium iodide solution (5 ml.) followed by methyl alcohol and ether. Yield 0·29 g.

Found : Cu, 23·3%.

Calculated : 23·3%.

SUMMARY.

Copper (I) iodide dissolves in concentrated ammonium or alkali bromide solution to form the bromo-iodo-cuprate (I) ion. Double decomposition of solutions containing this ion with solutions of tetrammine and bis-ethylenediamine copper (II) ions yields the corresponding tetrammine and bis-ethylenediamine copper (II) bromo-iodo-cuprates (I) of general formula $[Cu^{II}(A)_4][Cu^{I}IBr]_2$. Solutions containing the bromo-iodo-cuprate (I) ion give with ammonium hydroxide a compound of empirical formula $(CuI)_2.NH_3$, whose structure is unknown. With ethylenediamine, however, partial oxidation takes place and bis-ethylenediamine copper (II) bromo-iodo-cuprate (I) is obtained. Similarly solutions of the diiodo cuprate (I) ion yields with ammonia and ethylenediamine compounds of empirical formula $CuI.NH_3$ and $(CuI)_2.C_2H_4(NH_2)_2$ respectively. Possible structures for these compounds are suggested. Attempts to prepare diamine (ethylenediamine) copper (II) diiodo-cuprate (I) were unsuccessful.

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BIBLIOGRAPHY.

Biltz, W., and Stollenwerk, W., 1921, *Z. anorg. Chem.*, **119**, 97.

Harris, C. M., 1948. THIS JOURNAL, **82**, 218–224.

Horn, D. W., 1908. *Amer. Chem. J.*, **39**, 184.

Johnson, C. H., and Bryant, S. A., 1934. *J. Chem. Soc.*, 1783.

Mann, F. G., Purdie, D., and Wells, A. F., 1936. *J. Chem. Soc.*, 1503.

Morgan, G. T., and Burstall, F. H., 1926. *J. Chem. Soc.*, 2022.

Silberrad, O., 1905. *J. Chem. Soc.*, **87**, 67.

Wells, A. F., 1945. " Structural Inorganic Chemistry."   Oxford University Press, pp. 504–506.

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THE CHEMISTRY OF OSMIUM.

PART VII.   THE BROMO AND CHLORO PENTAMMINE OSMIUM III SERIES.

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With the exception of the osmyl ammines $OsO_2(NH_3)_4X_2$ (W. Gibbs, 1881), no complex compounds of osmium containing ammonia, pyridine or ethylene-diamine are known.

The curious substance potassium osmiamate $K(OsO_3N)$, a compound of octavalent osmium has been prepared by treatment of osmium tetroxide with ammonia and aqueous potassium hydroxide (Fritsche and Struve, 1847; L. Brizard, 1900). It reacts with hydrochloric acid with the liberation of chlorine and degradation to the sexavalent state to form $K_2(OsCl_5N)$, which is reducible with stannous chloride to potassium amino pentachloro osmate IV $K_2(Os.NH_2Cl_5)$ (Werner and Dinklage, 1901).

Attempts to prepare osmium ammines by reaction of potassium hexachloro or hexabromo osmate IV with aqueous ammonia led to hydrolysis, with the separation, ultimately, of a black precipitate of (presumably) osmium dioxide. Similarly, solutions of potassium hexachloro or hexabromo osmate III (Dwyer, McKenzie and Nyholm, 1945; Dwyer, Humpoletz and Nyholm, 1946) darkened in colour and also, ultimately, a black precipitate resulted. The molecules of arsine in tris-dimethylphenyl arsine tri-bromo-osmium could not be replaced by boiling the compound with alcoholic ammonia. Instead, partial replacement of the bromine atoms by hydroxyl occurred (unpublished observations of Barclay and Dwyer, 1948). By analogy with platinum, palladium, ruthenium and iridium it appeared probable that direct ammination could not be achieved in the tetravalent state, and consequently the osmium must be reduced to the strongly reducing trivalent or bivalent states and then treated with ammonia in the absence of both oxygen and water. It was thought possible that these conditions could be realised simultaneously by heating a tetravalent osmium compound in dry ammonia gas. If necessary, preheating of the gas could be arranged to provide various pressures of hydrogen by thermal dissociation of the ammonia. The initial experiments with potassium hexachloro and hexa-bromosmate IV were not successful, either no reaction occurring or complete reduction to osmium metal. However, with ammonium hexabromosmate IV, a sublimate of ammonium bromide was observed to form at 260°. When ammonia gas was passed over the compound in a small porcelain boat at 280° a further sublimate appeared with change of colour of the complex salt from dark red to brownish, and at 300° more ammonium bromide appeared and a silvery deposit of osmium remained.

The following changes appeared to occur :

$$(NH_4)_2OsBr_6 \rightarrow OsBr_4 + 2NH_3Br$$

$$OsBr_4 + NH_3 + H_2 \rightarrow [Os(NH_3)_5Br]Br_2 + NH_4Br$$

$$[Os(NH_3)_5Br]Br_2 \xrightarrow{+H_2} Os + NH_4Br + NH_3$$

The yields of the osmium ammine, however, were poor and the reaction difficult to control. The initial experiments carried out in an autoclave with one or two atmospheres pressure of ammonia were not successful. Eventually it was found necessary to subject the ammonium bromosmate to 7 or 8 atmospheres pressure for a short time and then reduce the pressure to 2 atmospheres. When then heated at 285° for $1\frac{1}{2}$ to 2 hours a quantitative conversion to almost white bromo pentammine osmium III bromide was found to have occurred. Although much of the gas must have been consumed in the reaction, at the end, the ammonia pressure was found to have barely altered. When the initial high pressure was applied to the ammonium bromosmate it was found to have dissolved to a red solution in liquid ammonia. With subsequent lowering of the pressure the liquid boiled away but must have left a loose addition compound $(NH_4)_2OsBr_6.x.NH_3$, which is apparently transformed to the ammine. This will be investigated further. Bromopentammine osmium III bromide $(Os(NH_3)_5)Br_3$, obtained as a light fawn coloured micro-crystalline powder by precipitation of the aqueous solution, had powerful reducing properties, reacting with silver nitrate to form a precipitate of the silver halide, and on warming reducing the excess to metallic silver. With bromine water, oxidation and precipitation of an orange osmium IV ammine resulted. These compounds will be discussed in subsequent papers.

The iodide, $[Os(NH_3)_5Br]I_2$, the nitrate $[Os(NH_3)_5Br].(NO_3)_2$, and the perchlorate $[Os(NH_3)_5Br](ClO_4)_2$ were obtained as light brown or fawn micro-crystalline powders by double decomposition. The reaction with silver chloride gave a mixture of the hydroxy pentammine chloride, $[Os(NH_3)_5OH]Cl_2$, and the bromopentammine chloride, $[Os(NH_3)_5Br]Cl_2$. The former compound was transformed to chloropentammine osmium III chloride by treatment with hydrochloric acid.

Morgan and Burstall (1936) noted a similar case of transformation of chloro-hydroxy-tetrammine ruthenium III chloride to dichlorotetrammine ruthenium III chloride.

Under 7–8 atmospheres pressure of ammonia gas, bromo-pentammine osmium III bromide was found to dissolve to a greenish solution. Evaporation of the liquid ammonia left a green substance, which appeared to be a mixture of the original compound and the hexammine $[Os(NH_3)_6]Br_3$. The reaction is being investigated.

Chloro pentammine osmium III chloride was obtained from ammonium chlorosmate in the same way as the bromo compound. The almost white microcrystalline powder had an acid reaction to litmus and partly replaced the covalent halogen atom by hydroxyl on heating the aqueous solution.

$$[Os(NH_3)_5Cl]Cl_2 + H_2O \rightarrow [Os(NH_3)_5OH]Cl_2 + HCl.$$

The lability of the chlorine atom, due to its ionic character, made the preparation of derivatives such as $(Os(NH_3)_5Cl)I_2$ impossible. The chloro compound was also more sensitive to atmospheric oxidation than the bromo compound. Specimens of the solid after 10–14 days exposure to the atmosphere had little reducing action on silver nitrate, and appeared to be almost completely transformed to $[Os(NH_3)_5Cl]Cl_2.OH$.

During the preparation of the chloro pentammine compound, it was found that, provided small samples of 0·1–0·3 g. of ammonium hexachlorosmate were used, complete transformation to the white pentammine occurred—but with larger amounts of the hexachlorosmate (0·5–1·0 g.) a mixture of white and yellow powders was obtained. The top crust and the edges of the reaction product were usually white, whilst the centre was brownish yellow. The yellow product was insoluble in 0·5 N hydrochloric acid but soluble in water. From

the brownish aqueous solution it was precipitated easily with hydrochloric acid and separated from the chloropentammine compound.

The formula of the anhydrous compound was found to be $Os_2(NH_3)_8NHCl_5$, I, or $Os(NH_3)_8NCl_5$, II. Three of the chlorine atoms were ionised, and on treatment with cold sodium iodide, the substance $[Os_2(NH_3)_8NHCl_2]I_3$ or $[Os(NH_3)_8NCl_2]I_3$ was obtained. The yellow substance had no reducing action on aqueous silver nitrate and thus presumably was a compound of Osmium IV. On heating in the autoclave with ammonia gas at 300° C., it was partially transformed to chloropentammine osmium III chloride.

$$\left[\begin{array}{cccc} & NH_3 & & NH_3 \\ NH_3 & | & & | & NH_3 \\ Cl-Os & -NH- & Os-Cl \\ NH_3 & | & & | & NH_3 \\ & NH_3 & & NH_3 \end{array} \right] Cl_3$$

$$I$$

$$\left[\begin{array}{cccc} & NH_3 & & NH_3 \\ NH_3 & | & & | & NH_3 \\ Cl-Os & -N= & Os-Cl \\ NH_3 & | & & | & NH_3 \\ & NH_3 & & NH_3 \end{array} \right] Cl_3$$

$$II$$

In the structural formula I, one Os atom is formally trivalent and the other quadrivalent. However, both atoms would probably have the same valence by reason of a resonance phenomenon. This should lead to an intense colour. The pale colour, especially of the solutions, is a possible objection to I. In the structure II both atoms are quadrivalent, and this formula is to be preferred by analogy with the nitrilo complexes $K_2[OsN.Cl_5]$. Owing to the difficulty of carrying out hydrogen analyses in the presence of osmium, it is not possible to distinguish analytically between I and II. The substance in aqueous solution reacted acid, with darkening of colour on standing, due probably to replacement of the covalent Cl atoms by hydroxyl.

Titration with silver nitrate potentiometrically also confirmed that three chlorine atoms were ionised. The titration value, however, was a little high, indicating that some of the covalent chlorine atoms were replaced. The conductivity assuming formula II, for $1 \times 10^{-3}M$ and $2 \times 10^{-4}M$ solutions was found to be 499 mhos.

<div style="text-align:center">EXPERIMENTAL.</div>

Bromopentammine Osmium III Bromide Monohydrate.

Ammonium bromosmate IV in two small platinum boats was suspended in the centre of a still autoclave fitted with a steel needle valve, and pressure gauge. A steel tube led through the head of the autoclave to near the bottom so that the ammonia gas could be used to sweep out the air. The air was displaced at approximately 0·5 at. of NH_3 gas by allowing the head of the autoclave to lift, then the head was screwed down and the full pressure of an ammonia cylinder (90–115 lb./sq. in.) applied for 20–30 mins. With excessive time of exposure to high pressure the boats tended to fill with liquid ammonia and overflow. The pressure was then reduced to 2 atmospheres and the autoclave heated in an oil bath with the external temperature adjusted to give 285° C. at the platinum boats. After 1½–2 hours the autoclave was removed from the oil bath and allowed to cool. The white powder left in the boats was ground up finely and extracted with warm dilute hydrobromic acid (approx. 0·1 N). The pale yellow solution was filtered from a small amount of dark substance, and ammonium bromide added. The pentammine precipitated as a pale fawn powder, and the precipitation was completed by cooling in ice. After washing with 90% alcohol the substance was dried over calcium chloride. On heating, the compound darkened considerably, leaving ultimately a deposit of osmium. It was insoluble in alcohol and acetone, but easily soluble in warm water. The density was found to be 2·49. The

equivalent conductivities of 1×10^{-3} and 2×10^{-4} M solutions were found to be 248 and 229 mhos., showing the compound to be a ternary electrolyte. On treatment with a slight excess of silver nitrate, followed by potentiometric titration with potassium chloride, almost all of the bromine appeared to have precipitated.

Found : Br$=42 \cdot 1\%$.

Calculated : Br$=30 \cdot 02\%$. Total Br$=45 \cdot 03\%$.

The osmium analyses were carried out in a micro porcelain boat by heating 2-8 mg. of the substance in oxygen-free ammonia gas up to a temperature of 460° C., and then weighing the osmium metal. This procedure was not suitable for the perchlorate or nitrate for which a colorimetric method (Dwyer and Gibson, 1950) was used.

Found : Os$=35 \cdot 6$; N$= 13 \cdot 0$; Br$= 44 \cdot 93\%$.

Calculated for [Os(NH$_3$)$_5$Br]Br$_2$1H$_2$O : Os$=35 \cdot 68$; N$= 13 \cdot 11$; Br$=45 \cdot 03\%$.

Bromopentammine Osmium III Iodide.

The bromopentammine bromide, in warm water, was treated with a little potassium iodide. The substance crystallised as sparingly soluble dark yellow micro prisms on scratching the sides of the vessel. The compound was washed with alcohol and dried at 100° C.

Found : Os$=31 \cdot 1\%$.

Calculated for [Os(NH$_3$)$_5$Br]I$_2$: Os$= 31 \cdot 23\%$.

Bromopentammine Osmium III Nitrate.

The bromopentammine bromide in warm water was treated with solid ammonium nitrate when the sparingly soluble nitrate of the complex crystallised in brownish yellow prisms. It was washed with 80% alcohol and dried at 100°. The substance decomposed at approximately 200° C. with a slight explosion and a black cloud of osmium metal.

Found : Os$=39 \cdot 3\%$.

Calculated for [Os(NH$_3$)$_5$Br](NO$_3$)$_2$: Os$=39 \cdot 7\%$.

Bromopentammine Osmium III Perchlorate Monohydrate.

This substance from sodium perchlorate and the bromopentammine bromide gave a brownish yellow sparingly soluble micro-crystalline powder. It exploded on heating.

Found : Os$=33 \cdot 27\%$.

Calculated for [Os(NH$_3$)$_5$Br](ClO$_4$)$_2$.H$_2$O : Os $33 \cdot 24\%$.

Bromopentammine Osmium III Hexabromosmate IV Dihydrate.

A solution of potassium hexabromosmate IV in dilute hydrobromic acid was added to an aqueous solution of the bromo pentammine bromide. The dark reddish brown microcrystalline precipitate was washed with alcohol and dried at 100° C.

Found : Os$=35 \cdot 62\%$.

Calculated for [Os(NH$_3$)$_5$Br](OsBr$_6$).2H$_2$O : Os$=35 \cdot 86\%$.

Bromopentammine Osmium III Hexachloroplatinate IV.

A solution of chloroplatinic acid was added to an aqueous solution of the bromopentammine bromide. The resulting orange yellow precipitate was washed with alcohol.

Found : Os$+$Pt : $46 \cdot 15\%$.

Calculated for [Os(NH$_3$)$_5$Br][PtCl$_6$].2H$_2$O : $46 \cdot 7\%$.

The Action of Silver Chloride in Bromopentammine Osmium III Bromide.

A saturated solution of the bromopentammine bromide at 35° C. was shaken with silver chloride for 5 minutes and then filtered. The pale yellow filtrate was precipitated with alcohol to yield a white colloidal suspension which was coagulated with concentrated hydrochloric acid. (This also served to hold traces of silver chloride in solution as the acid H.AgCl$_2$. Otherwise these traces were precipitated as, presumably, the pentammine osmium salt of the acid.) The

pale fawn substance was washed with 90% alcohol and dried at 100° C   It was very soluble in water and reduced silver nitrate to the metal on boiling. Found : Os$= 46 \cdot 2\%$. The bromopentammine osmium chloride requires Os$= 44 \cdot 6\%$. Another specimen prepared by longer shaking with silver chloride and allowed to stand overnight in the alcohol hydrochloric acid mixture gave Os$= 48 \cdot 1$. The chloropentammine osmium III chloride hemihydrate requires Os$= 48 \cdot 68\%$. Tests on this sample for bromine gave negative results. It was not possible to isolate the initial compound formed in the reaction between silver chloride and the bromopentammine bromide, since it could not be induced to coagulate without adding some contaminating ion. Specimens allowed to coagulate by long standing had undergone oxidation since they no longer reduced silver nitrate.

Chloropentammine Osmium III Chloride Hemihydrate.

Ammonium hexachlorosmate IV was heated in small platinum boats in ammonia gas as for the bromo compound (*vide supra*), except that the temperature was raised to 290-295°. At the end of the reaction the product consisted of a mixture of almost white material with a yellowish incrustation. With small quantities of ammonium hexachlorosmate ($0 \cdot 1-0 \cdot 2$ g.) the yellow material was almost absent. The mixture was ground up finely in a mortar and extracted three times with small amounts (10–15 c.c.) of $0 \cdot 5$ N HCl and filtered. The dark coloured precipitate was reserved (see later) and the pale yellow filtrate precipitated by the addition of alcohol. The resulting very pale fawn coloured powder was washed with alcohol, redissolved in the minimum of $0 \cdot 5$ N hydrochloric acid and traces of a yellow compound filtered off. It was then reprecipitated with alcohol and dried at 100° C. The substance was much more soluble in water than the bromo compound, the solution was acid (pH $4 \cdot 5$) due to partial replacement of the covalent halogen by hydroxyl. On reprecipitation from water with alcohol : found Cl $= 19 \cdot 95\%$; Os $= 53 \cdot 18\%$. Calculated for $[Os(NH_3)_5OH]Cl_2$: Cl$= 19 \cdot 54$; Os $= 54 \cdot 9\%$.

The chloropentammine chloride reduced warm silver nitrate to the metal rapidly but specimens of the solid after two or three weeks failed in this reaction and hence must have undergone oxidation.

Found : Os$= 49 \cdot 6$, $49 \cdot 04$, $48 \cdot 8$, $48 \cdot 6$, $48 \cdot 5$, $48 \cdot 8$ (on different preparations) ; N$= 18 \cdot 11$; Cl$= 27 \cdot 0$.

Calculated for $[Os(NH_3)_5Cl]Cl_2.\frac{1}{2}H_2O$: Os$= 48 \cdot 67$; Cl$= 27 \cdot 25$; N$= 17 \cdot 91\%$.

Dichloro-octammine-μ-nitrilo-diosmium Trichloride.

The residue from the extraction of the chloropentammine osmium III chloride with $0 \cdot 5$ N hydrochloric acid was extracted with water at 40° C. The resulting brownish orange solution was treated with hydrochloric acid, when it lost its brown colour becoming orange yellow and depositing a brownish yellow crystalline precipitate. This was filtered, washed with hydrochloric acid and alcohol and dried at 100°. The substance was found to be easily soluble in cold water, becoming brownish on heating. The solution, which had an acid reaction, precipitated the solid on the addition of hydrochloric acid or chloride ion. It gave a precipitate of silver halide on treatment with silver nitrate, but caused no reduction to the metal on boiling.

On standing over P_2O_5 or heating at 130° C., two molecules of water were lost without visible change in colour or form.

Found, undried substance : Os$= 50 \cdot 5$; N$= 16 \cdot 9$; Cl$= 23 \cdot 78\%$; H$_2$O$= 4 \cdot 2\%$.

Calculated for $Os_2(NH_3)_8N.Cl_5.2H_2O$: Os$= 51 \cdot 1\%$; N$= 16 \cdot 93$; Cl$= 23 \cdot 85$; H$_2$O$= 4 \cdot 8$.

Found, anhydrous substance : Os$= 53 \cdot 1$; N$= 17 \cdot 5$; Cl$= 25 \cdot 05$; Cl (ionised)$= 16 \cdot 8\%$.

Calculated for $Os_2(NH_3)_8N.Cl_5$: Os$= 53 \cdot 7$; N$= 17 \cdot 79$; Cl$= 25 \cdot 07$; Cl (ionised)$= 15 \cdot 04$.

Dichloro-octammine-μ-nitrilo-diosmium Tri-iodide.

The chloro compound above, in water, was treated with a few drops of hydrochloric acid to suppress hydrolysis and sodium iodide added. The resulting yellow brown precipitate was filtered off immediately, washed with alcohol and dried at 100°.

Found : Os$= 38 \cdot 6$; N$= 12 \cdot 9\%$.

Calculated for $[Os_2(NH_3)_8N.Cl_2]I_3$: Os$= 38 \cdot 8$; N$= 12 \cdot 81$.

Di-iodo-Octammine-µ-diosmium Trichloride.

The chloro compound in hot water containing hydrochloric acid was heated at 80° with excess sodium iodide and cooled. The brownish yellow microcrystalline precipitate was washed with hydrochloric acid and alcohol.

Found : Os=43·4 ; N=14·17%.

Calculated for $[Os_2(NH_3)_8NI_2]Cl_3$: Os=42·60 ; N=14·12%.

SUMMARY.

Ammonium hexabromo and hexachlorosmate IV reacted with ammonia gas under pressure at 280–300° C. with the formation of bromopentammine osmium III bromide, and chloropentammine osmium III chloride. These compounds were pale fawn solids soluble in water to pale yellow solutions, which reduced silver nitrate solution to the metal on boiling. The covalently attached halogens were labile, especially in the chloro compound, whose aqueous solution had an acid reaction due to the replacement of chlorine by hydroxyl.

The curious compound $Os_2(NH_3)_8N.Cl_5.2H_2O$ formulated dichloro-octammine-µ-nitrilo-diosmium trichloride was formed during the reaction of ammonium hexachlorosmate with ammonia.

ACKNOWLEDGEMENTS.

REFERENCES.

Brizard, L., 1900. *Ann. chim. Phys.*, **21**, 373.

Dwyer, F. P., and Gibson, N. A., 1950. *The Analyst*, in press.

Dwyer, F. P., McKenzie, H. A., and Nyholm, R. S., 1945. THIS JOURNAL, **79**, 183.

Dwyer, F. P., Humpoletz, J. E., and Nyholm, R. S., 1946. *Ibid.*, **80**, 242.

Fritsche, J., and Struve, H., 1847. *J. prakt. Chem.*, **41**, 97.

Gibbs, W., 1881. *J. Am. Chem. Soc.*, **3**, 238.

Morgan, G. T., and Burstall, F. H., 1936. *J. Chem. Soc.*, **41**.

Werner, A., and Dinklage, K., 1901. *Ber.*, **34**, 3702.

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THE CHEMISTRY OF IRIDIUM.

PART V. THE OXIDATION OF IRIDIUM III SALT SOLUTIONS.

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and (MISS) E. C. GYARFAS, M.Sc.

This study has been undertaken as a preliminary to the investigation of the fluorides of iridium, in which the bond Ir–F may be expected to be predominantly ionic. The nitrates, perchlorates and, to a lesser extent, the sulphates, can be expected to be ionic and hence likely to give useful information concerning the fluorides.

Little is known of the simple salts of tetravalent iridium such as the nitrate, sulphate and perchlorate, attention having been confined almost exclusively to the covalent chloride and bromide, and to various complex compounds, of which the hexahalogenates R_2IrCl_6 are the best defined. It has been noted very long ago (Le de Boisbaudron, 1883 ; Marino, 1904) that the yellow solutions of iridium III sulphate, $Ir_2(SO_4)_3$, became green or blue on standing in air, and the colour change has been ascribed to the existence of varying amounts of salts in higher oxidation states. Similarly, the nitrate, prepared by dissolution of iridium III hydroxide in dilute nitric acid, can be obtained as a yellow solution, which rapidly becomes blue on standing or warming. Although the substance responsible for the blue colour has not been isolated it has been generally inferred that a higher oxidation state than trivalent iridium is present.

In the present work solutions of iridium III hydroxide in sulphuric, perchloric and nitric acids have been potentiometrically titrated with a variety of oxidising agents, or oxidised anodically and potentiometrically reduced. All of the iridium III salt solutions were oxidisable by bromine water with the development of a blue colour, discharged by the addition of ferrous sulphate. After such oxidation and reduction, however, the solutions became extremely sensitive to oxidation by air and became blue very rapidly. It could be shown that the enhanced oxidisability was not due to catalysis by iron salts or bromide ion, and hence must be ascribed to a new ionic species in the iridium III solutions. As the acid concentration of the solutions was reduced, it was found that oxidation became easier, whilst, on the other hand, if sufficient acid was present, bromine failed· to effect any oxidation. These observations suggested that the easily oxidised ion is not the simple hydrated Ir^{+++} but probably an oxy or hydroxy ion of the type IrO^+ or $Ir(OH)^{++}$. This ion is formed directly by the reduction of the blue oxidised solutions, or may occur by hydrolysis :
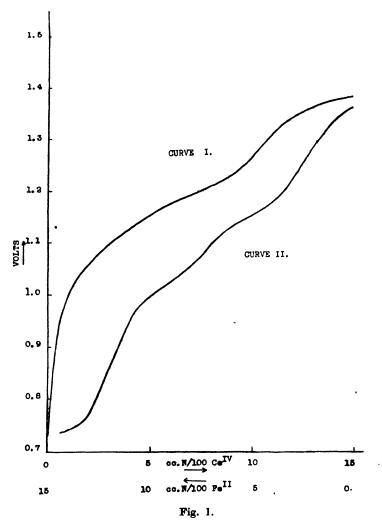
$$\left\{ \begin{array}{l} Ir^{+++} + H_2O \rightarrow IrO^+ + 2H^+ \\ Ir^{+++} + H_2O \rightarrow Ir(OH)^{++} + H^+ \end{array} \right.$$

The existence of ions of this type in solution is consistent with the occurrence of basic salts such as $Ir(OH)SO_4$, and the amphoteric character of the oxide, Ir_2O_3 .

When titrated potentiometrically with cerium IV salts or potassium permanganate the resulting curves showed an initial very sharp rise in the potential

due to the oxidation of Ir^{III} to Ir^{IV}, followed by the usual flattening and a sharp potential increase at approximately 1·27 volts.   This signalised the end of the reaction $Ir^{III} \to Ir^{IV} + e'$, and the commencement of the reaction $Ir^{IV} \to Ir^{VI} + 2e'$. The latter reaction was incomplete at the maximum potential available from the oxidising agent.

However, if the oxidised solutions were reduced with ferrous sulphate quite different curves were obtained, showing three potential breaks.   The additional

Fig. 1.
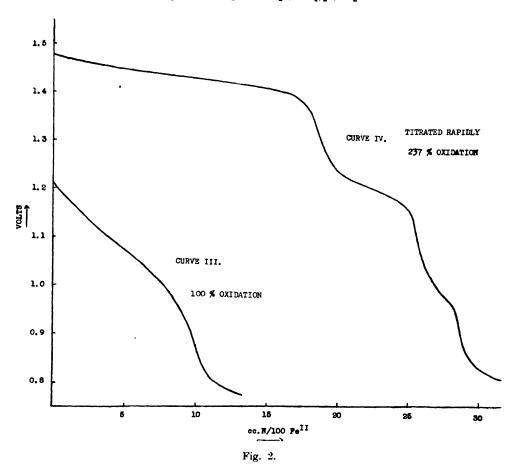
end point occurring at approximately 1·1 volts, as will be shown later, is not due to reduction of Ir^{VI} to the unknown valency state Ir^{V}, but to an unstable form of Ir^{IV}, which arises only by reduction of Ir^{VI} and cannot be obtained by oxidation of Ir^{III} (Curves I, II).

The anodic oxidation of iridium III salts in nitric, perchloric and sulphuric acids gave progressively green, blue, violet, brown violet and finally brown solutions.   The last stage, which involved the formation of an iridium VI compound, could be reached only in acid concentrations above 3 normal, with high current densities on a clean polished platinum anode.   In solutions of

lower acidity the anode became covered with a brownish blue deposit of (presumably) iridium trioxide and the oxidation of the solution stopped at the violet stage of iridium IV, which was also the ultimate oxidation that could be achieved with low current densities, or roughened electrodes.

It is significant that the brownish deposit on the anode was not formed in strongly acid solution, and it is suggested that, in the presence of sufficient acid, the oxide IrO_3 may react to form salts of the cation $IrO_2{}^{++}$

$$IrO_3 + 2HClO_4 \rightarrow IrO_2.(ClO_4)_2 + H_2O.$$

Fig. 2.
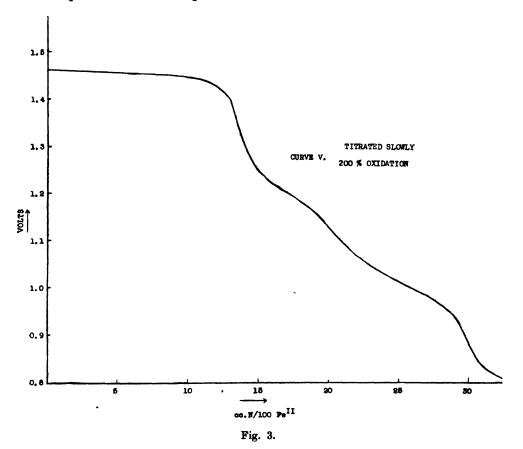
Such salts are analogous to the osmyl salts $OsO_2.X_2$, and the well known uranyl salts $UO_2.X_2$.

When the violet solutions were titrated potentiometrically with ferrous sulphate solution, the curves showed only one step due to the reduction of iridium IV to iridium III (Curve III). The brown solutions, when titrated rapidly, gave curves showing three steps ; but, if titrated very slowly, only two steps (Curves IV, V). From the total percentage oxidation of the brown solutions and the width of each of the steps (i.e. the titration value), it could be shown that the first reduction step, in the rapidly titrated solutions, was from iridium VI to an unstable form of iridium IV, and not to the unknown valency state of five ; the second, the reduction of the unstable form of iridium IV to iridium III ; and the last step, the reduction of the stable form of iridium IV

to iridium III. In the slow titration, the potential break at the end of the reduction of iridium VI was very much larger, and the step due to the reduction of the unstable form of iridium IV disappeared.

Provided that the oxidation was not carried beyond 100 per cent. (*i.e.* Ir^{IV}) the unstable form of iridium IV could not be detected on the curves, and where the oxidation was carried to the hexavalent stage, the width of the step due to the unstable form was proportional to the amount of iridium VI present. It is concluded, therefore, that the unstable tetravalent state can only arise by reduction of the hexavalent state. The maximum oxidation achieved in these experiments was 273 per cent.

Fig. 3.

If the assumption is made that the unstable form of quadrivalent iridium carries the larger charge, and then the charge is reduced by hydrolysis to the stable form of the quadrivalent state, the following scheme is consistent with the results obtained.

$$\begin{cases} IrO_2{}^{++} \text{ (Brown)} +2H^+ +2e' \rightarrow H_2O +IrO^{++} \text{ (Red violet)} \\ IrO^{++} +H_2O \rightarrow [IrO.OH]^+ +H^+ \text{ (Blue violet)} \end{cases}$$

$$\begin{cases} IrO^{++} +H^+ +e' \rightarrow [Ir(OH)]^{++} \text{ (Yellow)} \\ [IrO.OH]^+ +2H^+ +e' \rightarrow H_2O +[Ir(OH)]^{++} \end{cases}$$

In weakly acid solutions the blue violet solutions of the stable form of quadrivalent iridium yield a very fine precipitate of iridium dioxide.

$$[IrO.OH]^+ \rightarrow IrO_2 +H^+$$

The oxidation from Ir^{III} proceeds

$$Ir^{+++} \rightarrow [IrOH]^{++} \rightarrow [IrO.OH]^+ \rightarrow IrO_2^{++}$$

Although dark violet blue solid crystalline substances have been obtained by the oxidation of iridium III nitrate, sulphate and perchlorate, none of the preparations has been obtained in a pure state. The work on the isolation of these compounds is proceeding.

In a subsequent paper the redox potentials of the Ir^{III}/Ir^{IV} and Ir^{IV}/Ir^{VI} couples will be discussed.

EXPERIMENTAL.

Iridium III Salt Solutions.

Potassium hexachloriridate IV (1·2 g.) was dissolved in 50 ml. of water at 80° C. and whilst hot treated with sodium hydroxide solution (0·40 g. in 50 ml. of water). The mixture was adjusted with dilute alkali until faintly alkaline, and maintained near the boiling point to cause the blue precipitate of hydrated iridium dioxide to granulate. This was removed by centrifuging, washed with hot water until it commenced to peptise and then dissolved by heating with a mixture of 20% sulphuric acid (20 ml.), 5% sulphurous acid (20 ml.), and water (30 ml.). The mixture was boiled down to half the volume to expel all sulphur dioxide, and the greenish blue solution of iridium III sulphate centrifuged to remove traces of undissolved iridium IV and iridium III oxides.

The solution of the sulphate was diluted to 50 ml. with water, and, keeping the temperature below 40° C., cold 10% sodium hydroxide was added until the initial precipitate of iridium III basic sulphate and hydroxide was just dissolved. The greenish yellow solution of sodium iridate III was cooled to room temperature, and the pH adjusted to approximately 6·5 with dilute sulphuric acid. The yellowish precipitate was centrifuged and washed once with cold water. By dissolving in cold normal sulphuric acid and making the volume to 200 ml. an approximately 0·01 M solution of the sulphate resulted.

The iridium III perchlorate was made in the same way, using normal perchloric acid to dissolve the precipitate. The hydroxide was reprecipitated with sodium hydroxide and re-dissolved. The last traces of sulphates were removed by the addition of a few drops of barium perchlorate solution. The nitrate was prepared the same way. All of the solutions became greenish and finally blue on standing. The nitrate became very dark blue in a few hours.

The iridium content in all solutions was found by evaporation of a known volume to dryness, followed by ignition to the metal. Traces of sodium salts were washed from the ignited metal with hot dilute hydrochloric acid.

The Potentiometric Oxidation of Iridium III Salts.

The potentiometric set-up was similar to that used in previous work (Dwyer, Nyholm and McKenzie, 1944). The mixture at 25° C. was stirred mechanically in a current of purified carbon dioxide during the titration with approximately N/100 potassium permanganate, cerium IV sulphate, nitrate or perchlorate as oxidising agents, or ferrous sulphate for the back titration of the oxidised solutions. In all titrations the initially yellow or greenish yellow solutions became green, blue and finally bluish violet. In the back titration, except in strongly acid solutions, these colour changes were not entirely reversed, and a pale blue colloidal suspension of iridium dioxide was left at the end.

Substantially the same results were obtained with all of the oxidising agents, at acid concentrations from 0·5 N to 6 N, showing a potential break at approximately 1·27 volts. From the volume of oxidising agent used, this corresponded to the end of the oxidation Ir^{III}—e$'$→Ir^{IV}. (Curve I.) Further addition of oxidising agent involved only partial oxidation to the hexavalent state.

The reduction curves with ferrous sulphate gave typical curves involving potential breaks at 1·27 volts, 1·1 volts and 0·9 volt. The break at 1·1 volts was usually poorly defined.

The Anodic Oxidation.

The anodic oxidation cell consisted of a small beaker (30 ml.) containing a cylinder of smooth polished platinum, which fitted the beaker so closely that the inner side of the cylinder could be considered as the effective anode surface. A small sintered glass crucible with the base removed, and fitting loosely into the platinum cylinder, contained the platinum wire cathode. The solution to be oxidised containing the appropriate amount of acid was placed in the beaker, and the cathode chamber was filled with acid of the same concentration ; the levels in the two chambers being adjusted so that the cathode level was slightly higher. The solution being oxidised was stirred with a rapid stream of fine carbon dioxide bubbles. When oxidation was complete, the cathode was removed, the porous membrane washed out by allowing some of the cathode liquid to percolate through ; then the rest of the cathode acid added, and the anode washed with a little further acid. The solution was then made up to a specified volume.

The percentage oxidation achieved was determined by taking a known volume of solution, diluting with water, adding excess potassium iodide, and titrating the liberated iodine with sodium thiosulphate. From the known iridium content of the solution before oxidation, the calculation can then be made. A small correction was necessary for the iridium deposited on the cathode.

In the sulphate solutions, persulphate was formed during the oxidation making the estimation of the percentage oxidation impossible, whilst the nitric acid in the nitrate solutions interfered with the titration by slowly liberating iodine. For these reasons, beyond qualitatively establishing that the same products are formed in sulphate and nitrate solutions, the work has been restricted to the perchlorate.

It was found that provided the current was more than $0 \cdot 2$ amp. (6 V. applied), or the current density of more than $2 \cdot 6 \times 10^{-3}$ amp./sq. cm., the extent of oxidation was a function of the time and the state of the electrode surface. With roughened electrodes, or electrodes that had been used previously without cleaning, gassing occurred and the oxidation could not be carried much beyond the Ir^{IV} state. The electrode between experiments was cleaned by making it the anode in 5 N sulphuric acid and passing a current of 4–5 amps. for twenty minutes. Table I shows the results obtained by oxidising in 4 N perchloric acid with a current of $0 \cdot 5$ amp. ($6 \cdot 5 \times 10^{-3}$ amp./sq. cm. of anode surface).

TABLE 1.

$0 \cdot 0150$ gm. of Ir in 10 ml. solution.

Time in Minutes.	Loss on Cathode. Grammes.	Total Ir. Grammes.	N/100 $Na_2S_2O_3$. Millilitres.	Percentage Oxidation.	Percentage Ir^{VI}.
10	$0 \cdot 0006$	$0 \cdot 0144$	$15 \cdot 9$	110	$5 \cdot 0$
20	$0 \cdot 0012$	$0 \cdot 0138$	$24 \cdot 2$	175	$37 \cdot 5$
40	$0 \cdot 0022$	$0 \cdot 0128$	$27 \cdot 4$	214	$57 \cdot 0$
90	$0 \cdot 0029$	$0 \cdot 0121$	$29 \cdot 3$	242	$71 \cdot 0$

The potentiometric reduction of the anodically oxidised solutions was carried out in the assembly described above, with approximately N/100 ferrous sulphate solution. Typical reduction curves of solutions oxidised to various stages are shown in Figures 1 to 3.

SUMMARY.

The oxidation of iridium III sulphate, perchlorate and nitrate with potassium permanganate, or cerium IV salts yields bluish violet solutions, which probably contain the cation $[IrO.OH]^+$. The anodic oxidation yields bluish violet solutions, which contain the same ion, or the oxidation can be carried to the stage of iridium VI, which exists in the solution as the brown ion IrO_2^{++}.

By examination of the potentiometric reduction curves of the brown solutions, it is concluded that an unstable form of quadrivalent iridium, probably

as the reddish violet ion IrO^{++}, is the first reduction product of the ion IrO_2^{++}. The unstable ion rapidly changes to the stable $[IrO.OH]^+$, and can be obtained only by the reduction of iridium VI.

REFERENCES.

Dwyer, F. P., McKenzie, H. A., and Nyholm, R. S., 1944. THIS JOURNAL, **78**, 260.

Le de Boisbaudron, 1883. *Compt. Rend.*, **96**, 1336, 1406, 1551.

Marino, L., 1904. *Zeit. anorg. Chem.*, **42**, 213. See also Delepine, M., 1927. *Zeit. Phys. Chem.*, **130**, 222.

PHYSICAL INVESTIGATIONS ON COMPLEXES OF DIPHENYLTHIOCARBAZONE.

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The object of this investigation was to study the interaction of metal complexes of diphenylthiocarbazone with metal ions, in order that information concerning the strength of the binding of the metal to the ligand, diphenyl-thiocarbazone, and the extent of the exchange between metal ions in solution with metal atoms bound to this ligand could be obtained.

Previous investigations by Maley and Mellor (1949) on the stability of a series of metal complexes have shown that the order of the stability constants for metal chelates with a series of ligands was independent of the chelating organic molecules investigated.

If one metal complex is more stable than another of the same type, it should be possible under suitable conditions for one metal to displace another metal from a less stable complex.

The reaction

$$(\text{ligand})_n \text{Me}_1 + \text{Me}_2 \rightleftharpoons (\text{ligand})_n \text{Me}_2 + \text{Me}_1$$

should therefore proceed and displace the original metal Me_1 from its complex if Me_2 forms a more stable complex with the ligand.

Diphenylthiocarbazone, which is acidic in character and forms chelates with many metals, exists in both the keto and enol form.

keto   enol

According to Fisher (1934) the keto form reacts with metal ions. The imino hydrogen atom is replaced by the metal atom, which is then coordinatively bound to the nitrogen. These complexes are soluble in organic solvents and as a rule are coloured.

The reagent diphenylthiocarbazone is itself insoluble in water and dilute mineral acids but is soluble in chloroform, carbon tetrachloride, and alcohol.

A chloroform mixture of the uncombined chelate and the chelate combined with the metal ion can be separated by a dilute aqueous ammonia solution (0·02 M), which extracts the uncombined complex diphenylthiocarbazone leaving the pure colour of the metal complex in the chloroform layer.

METHOD OF INVESTIGATION OF THE REACTION.

In the present investigation the following specific exchange reactions were studied :

$$Zn(diphenylthiocarbazone) + Me \rightleftharpoons Me(diphenylthiocarbazone) + Zn$$

where Me=Cu, Co and Zn.

The extent to which this reaction proceeds from left to right was noted by using radioactive ions. The zinc atoms in each case were labelled by using radioactive zinc solutions.

The reagent, diphenylthiocarbazone, which is a spot reagent and used for determining metal ions in concentrations 1γ to 100γ, is very sensitive to trace metal ions and this factor necessitated the taking of special precautions to ensure that all apparatus and reagents were free of zinc and other trace metals before proceeding.

EXPERIMENTAL.

Reagents.

Diphenylthiocarbazone B.D.H. quality was used throughout and found free of oxidised products.

Trace elements were eliminated from the pyrex glassware by thorough cleaning, washing and testing it with diphenylthiocarbazone reagent until free of metal ions. No grease or lubricant (other than water) or rubber fittings could be used on the separating funnels as all these were found to contain a significant amount of zinc.

The distilled water and absolute alcohol and ammonia were redistilled several times in pyrex glassware and the chloroform purified by distilling under a cover of aqueous solution of sodium thiosulphate containing a little NaOH, drying the distillate over $CaCl_2$ and redistilling.

Preparation of Zinc Diphenylthiocarbazone.

It was prepared by adding diphenylthiocarbazone chloroform reagent (15 milligrammes in 100 ml. $CHCl_3$) to the dilute 50γ aqueous zinc chloride at pH 7·0. The excess reagent was removed by extracting it with dilute (0·02 M) aqueous ammonia until the upper layer was water clear.

The red complex remains in the chloroform layer. It was made up as required because the colour fades on standing due to slow oxidation.

The formation of metal diphenylthiocarbazone is influenced by the hydrogen ion concentration of the aqueous solution [Fisher and Leopolidi (1934), Fisher (1934), Hibbard (1937), White (1936)].

The percentage of zinc ions extracted from an aqueous solution by a chloroform diphenylthiocarbazone solution varies considerably with pH. The partition effect in dilute solutions is illustrated by Fig. 1 (Hibbard, 1937).

The exchange reactions were therefore carried out experimentally at the constant pH of 7·0.

Alcoholic zinc diphenylthiocarbazone was prepared by evaporating the chloroform solution to a low bulk and then diluting with absolute alcohol giving a one-phase solution.

Exchange Reactions.

The alcohol zinc diphenylthiocarbazone was mixed with approximately an equal volume of solution of the metal salt solution at the same molar concentration and at pH 7·0, so that

$$\frac{[\text{Zinc complex}]}{[\text{Metal salt conc.}]} \sim 1$$

The zinc complex was then separated from the metal solution by adding $CHCl_3$. The $CHCl_3$ layer was washed with water and the water layer washed with $CHCl_3$. Both layers were then diluted, an aliquot portion taken, evaporated and dried on a glass counting plate and their respective radioactivity measured on a Geiger Muller counter with a scale of eight using a β tube with a two-inch lead shielding and a thin mica window.

No self adsorption corrections were needed due to the relative high energy of the β and γ rays emitted from Zn* 65 used, and, due to its relatively long half life of 250 days, no decay corrections were required.

Due to the fact that emission of radioactive radiations follow statistical laws of random processes the statistical probable error in the recorded activity is given by Poisson's Term, $0 \cdot 6745 \sqrt{A^1}$, where A^1 is the number of events recorded.

The activity of the sample was then determined as follows :

Average sample+background count $= B \pm 0 \cdot 6745 \ \sqrt{B}$

Average sample count $\doteq$ $B - A \pm \sqrt{(0 \cdot 6745 \sqrt{B})^2 + (0 \cdot 6745 \sqrt{A})^2}$

where A is the average background count.
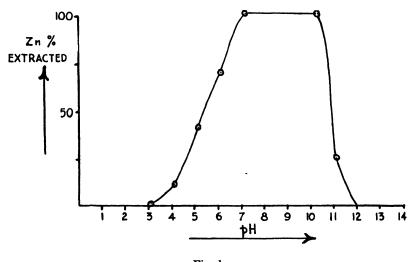
Fig. 1

The concentration of the metal ions in the aqueous phase was determined by separating the water layer, converting it into the diphenylthiocarbazone complex in chloroform and using a Klett photometer to determine its concentration.

In the copper and cobalt exchange reactions copper sulphate and cobalt nitrate solutions were added to the zinc complex solutions and allowed to stand several hours. The separation was then effected as above by adding chloroform and the activities of the two layers were measured. In both cases the activity of the aqueous solution increased to 100% of the original complex activity, indicating a complete exchange of the zinc atoms in the complex with the copper and cobalt ions.

The reaction between zinc atoms in the complex and zinc ions in solution was studied in the first instance by using active complex and inactive zinc ions, and secondly inactive complex and active zinc ions.

The relative concentrations of the zinc in both layers were then compared with the corresponding activities and were found to agree.

The exchange rate for the zinc-zinc exchange was very rapid in the alcoholic aqueous solution and within the minimum time required to separate the solutions ½ to 1 minute the activity of the aqueous layer reached 50% of the total activity, which means there is a 100% exchange of the zinc ions in solution with zinc atoms in the complex.

ACKNOWLEDGEMENTS.

SUMMARY.

There is a rapid exchange between zinc ions in solution with zinc atoms in zinc diphenylthiocarbazone and the zinc atoms are held by relatively weak bonds to the ligand.

Copper and cobalt metals form relatively stronger bonds with the ligand and are more stable than the corresponding zinc diphenylthiocarbazone complex.

REFERENCES.

Fisher, H., 1934. *Z. Angew. Chem.*, **47**, 685.

Fisher, H., and Leopolidi, 1934. *Z. Anal. Chem.*, **97**, 385.

Hibbard, P. H., 1937. *Ing. Eng. Chem.*, **9**, 127.

Maley, L. E., and Mellor. D. P., 1949. *Aust. J. Sci. Res.*, **A 2**, 92.

White, W. E., 1936. *J. Chem. Education*, **13**, 369.

TABLES FOR NEARLY PARABOLIC ELLIPTIC MOTION.*

By HARLEY WOOD, M.Sc.

In this article tables are given for the representation of nearly parabolic elliptic Keplerian motion based on the formulæ of a previous paper (Wood, 1950a).

Equation (9) of that paper may be written

$$D_1 = 6k(1+e)^{3/2}q^{-3/2}t = (1+e)6\mu + \mu^3 6 \left\{ \frac{\sin^{-1}\varepsilon^{1/2}\mu - \varepsilon^{1/2}\mu}{\varepsilon^{3/2}\mu^3} \right\}, \quad \dots\dots\dots \quad (1)$$

where k is the Gaussian constant, e the eccentricity, $\varepsilon = (1-e)/(1+e)$, $\mu = y_0/q$, $\lambda = x_0/q$ and x_0, y_0 are the rectangular coordinates in the plane of motion with the x_0 axis directed towards perihelion. When the place in the orbit is known, and hence one of the alternatives

$$\mu = (\sin E)/\varepsilon^{1/2} = y_0/q = (r \sin v)/q$$

calculable, this formula may be used to calculate perihelion time. The coefficient of μ^3,

$$6 \left\{ \frac{\sin^{-1}\varepsilon^{1/2}\mu - \varepsilon^{1/2}\mu}{\varepsilon^{3/2}\mu^3} \right\} = A$$

is given in Table 1 with argument $\varepsilon^{1/2}\mu$. The table was calculated to nine decimal places using the series when $\varepsilon^{1/2}\mu \leqslant 0.20$ and thereafter the *Table of Arc sin x* prepared by the " Mathematical Tables Project " (1945). The values of A, and the remaining functions of this article, were calculated at ten times the interval given and then sub-tabulated to the interval of the table, the intention being that errors should not exceed 0.52 unit of the last recorded place.

In order to provide for iterative computation of μ from equation (1) and of velocities facilities are given for convenient calculation of

$$\frac{dD_1}{d\mu} = 6(1+e) + \frac{6}{\varepsilon} \left\{ \frac{1}{(1-\varepsilon\mu^2)^{1/2}} - 1 \right\}$$

$$= 6(1+e) + \mu^2 6 \left\{ \frac{1-(1-\varepsilon\mu^2)^{1/2}}{\varepsilon\mu^2(1-\varepsilon\mu^2)^{1/2}} \right\}.$$

$$I = 6 \left\{ \frac{1-(1-\varepsilon\mu^2)^{1/2}}{\varepsilon\mu^2(1-\varepsilon\mu^2)^{1/2}} \right\}$$

is given in Table 1 and a correction to an approximate value of μ may be obtained by the formula

$$\triangle\mu = \{D_1 - 6(1+e)\mu - A\mu^3\}/\{6(1+e) + I\mu^2\}. \quad \dots\dots\dots \quad (2)$$

For obtaining μ from the known elements of the orbit tables are given for the use of formulæ (23) of the previous paper. Repeating these in a form adapted to the present purpose we have

$$D=[12k(1+e)^{1/2}q^{-3/2}c]t$$

where

$$c^2=1+\gamma_1\varepsilon+\gamma_2\varepsilon^2+\ldots,$$

$12k=0\cdot2064\ 2519$, c is obtained from Table 2 and the coefficient of t in the square brackets can be computed for the whole orbit.

Also

$$D=12c\sigma+c^3\sigma^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$\mu=\sigma\left\{\begin{matrix}1+g_{12}\varepsilon\sigma^2+g_{22}\varepsilon^2\sigma^2+g_{32}\varepsilon^3\sigma^2+\ \cdots\cdots\\+g_{24}\varepsilon^2\sigma^4+g_{34}\varepsilon^3\sigma^4+\cdots\cdots\\+g_{36}\varepsilon^3\sigma^6+\cdots\cdots\\\cdots\cdots\cdots\cdots\end{matrix}\right\}$$

Now writing

$$J=1+g_{12}\varepsilon\sigma^2+g_{24}\varepsilon^2\sigma^4+g_{36}\varepsilon^3\sigma^6+\ldots,$$

$$h=\varepsilon+\frac{g_{32}}{g_{22}}\varepsilon^2+\frac{g_{42}}{g_{22}}\varepsilon^3+\ldots$$

and

$$-K=g_{22}\varepsilon\sigma^2+g_{34}\varepsilon^2\sigma^4+g_{46}\varepsilon^3\sigma^6+\ldots.$$

we have

$$\mu=\frac{c\sigma}{c}\{J-hK+R\}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where R is a function of ε and μ defined by the equation.

Inserting the values of the coefficients we have

$$c^2=1-0\cdot8\varepsilon\ \ -0\cdot03428\ 57143\varepsilon^2\ \ -0\cdot01980\ 9524\varepsilon^3\ \ -0\cdot01323\ 4385\varepsilon^4$$
$$-0\cdot00963\ 4\varepsilon^5\ \ -0\cdot00742\varepsilon^6\ \ -0\cdot0059\varepsilon^7,$$

$$J=1\cdot0-0\cdot15\varepsilon\sigma^2\ \ +0\cdot00071\ 42857\varepsilon^2\sigma^4\ \ +0\cdot00003\ 96825\varepsilon^3\sigma^6$$
$$+0\cdot00000\ 24930\varepsilon^4\sigma^8\ \ +0\cdot00000\ 01683\varepsilon^5\sigma^{10},$$

$$K=+0\cdot00285\ 7143\varepsilon\sigma^2\ \ -0\cdot00112\ 6984\varepsilon^2\sigma^4\ \ -0\cdot00005\ 1252\varepsilon^3\sigma^6$$
$$-0\cdot00000\ 2454\varepsilon^4\sigma^8\ \ -[0\cdot000033\varepsilon^5\sigma^{10}],$$

$$h=1\cdot0\varepsilon\ \ +0\cdot57777\ 7778\varepsilon^2\ \ +0\cdot38600\ 2886\varepsilon^3\ \ +0\cdot28097\ 7689\varepsilon^4$$
$$-[2\cdot2\varepsilon^5],$$

where the terms in the brackets are not determined like the others but are empirical terms added to reduce the value of R. Their greatest effect on hK within the range of the table is 40 units in the ninth decimal place. Using the manuscript tables calculated from the above series to two places beyond what is recorded here, values of R were calculated from equation (4), μ first having been obtained from equation (2). The " Table of Values of R " gives the values found in units of the ninth decimal place, including errors of computation up to two units involved in using the full nine figures. R is negligible in seven figure work.

Table of Values of R *in Units of the Ninth Decimal Place.*

$\varepsilon^{\frac{1}{2}}\sigma$ \ ε	0·02	0·04	0·06	0·08	0·10
0·1	+1	+1	0	0	+1
0·2	0	+1	+1	0	−2
0·3	0	0	+1	0	−2
0·4	0	+2	+3	+2	−1
0·5	0	+2	+5	+6	+6
0·6	−2	−1	+3	+6	+5

The values of c and h are found, once for the orbit, from Table 2 ; $c\sigma$ is obtained from equation (3) using tables of parabolic motion (Wood, 1950b), and J and K come from Table 3 with argument $[\varepsilon^{1/2}c^{-1}]c\sigma$. When second differences are appreciable they may be allowed for by using the table with argument n and $\triangle_0'' + \triangle_1''$, published in the *Nautical Almanac for* 1937 and reprinted in the *Interpolation and Allied Tables.*

Having μ, we require

$$\lambda = 1 - \frac{1}{2(1+e)}\mu^2 \left\{ \frac{2 - 2(1-\varepsilon\mu^2)^{1/2}}{\varepsilon\mu^2} \right\},$$

which is equation 6 of the first paper. The quantity

$$\frac{2 - 2(1-\varepsilon\mu^2)^{1/2}}{\varepsilon\mu^2} = N$$

is given in Table 1 with argument $\varepsilon^{1/2}\mu$.

The formulæ for the rectangular equatorial heliocentric coordinates are then

$$x = [A_x] - \left[\frac{A_x}{2(1+e)}\right] N\mu^2 + [B_x]\mu,$$

$$y = [A_y] - \left[\frac{A_y}{2(1+e)}\right] N\mu^2 + [B_y]\mu,$$

$$z = [A_z] - \left[\frac{A_z}{2(1+e)}\right] N\mu^2 + [B_z]\mu,$$

where A_x, B_x . . . have the same meaning as in the second paper (Wood, 1950b) and the coefficients in the square brackets are precomputed.

As an illustration, using the conventional example from Gauss' *Theoria Motus,* we take

$e = 0·9676\ 4567,$ $q = 0·5829\ 751,$

$v = 100°,$ $\tan\ v = -5·671282,$

$\mu = (r\ \sin\ v)/q = 2·3291\ 134.$

The preliminary calculations of the constants required to compute either perihelion time or an ephemeris place give

$\varepsilon = 0·0164\ 4317,$ $6k(1+e)^{3/2}q^{-3/2} = 0·6399\ 971,$

$\varepsilon^{1/2} = 0·1282\ 309,$ $6(1+e) = 11·8058\ 740,$

$c = 0·9933\ 962,$ $12k(1+e)^{1/2}q^{-3/2}c = 0·6462\ 248,$

$\varepsilon^{1/2}c^{-1} = 0·1290\ 833,$ $h = 0·01660.$

For calculation of perihelion time we obtain

$$\varepsilon^{1/2}\mu = 0 \cdot 2986\ 643, \qquad\qquad A = 1 \cdot 0424\ 100,$$
$$t = 63 \cdot 54399\ \text{days}.$$

A many-figure calculation gives $t = 63 \cdot 5439\ 858$ days.

In calculating an ephemeris place with $t = 63 \cdot 543986$ days we obtain

$$c\sigma = 2 \cdot 3459\ 994, \qquad\qquad \mu = 2 \cdot 3291\ 135,$$
$$\varepsilon^{1/2}\sigma = 0 \cdot 3028\ 293, \qquad\qquad \varepsilon^{1/2}\mu = 0 \cdot 2986\ 643,$$
$$J = 0 \cdot 9862\ 502, \qquad\qquad N = 1 \cdot 0233\ 538,$$
$$K = 0 \cdot 0002\ 525, \qquad\qquad \lambda = -0 \cdot 4106\ 856$$

and for comparison with the original data we give

$$\tan v = \mu/\lambda = -5 \cdot 671281, \qquad\qquad v = 100°\ 00'\ 00'' \cdot 01.$$

REFERENCES.

Mathematical Tables Project, 1945.   Table of Arc sin x, Columbia University Press, New York.

Wood, H., 1950a.   This Journal, 83, 150.   Also Sydney Obs. Papers No. 10.

——————1950b.   This Journal, 83, 181.   Also Sydney Obs. Papers No. 11.

TABLE 1.

$\epsilon^{\frac12}\mu$	A 1·	I 3·	N 1·	$\epsilon^{\frac12}\mu$	A 1·	I 3·	N 1·
0·000	0000 000$_{4}$	0000	0000 000^{2}	0·050	0011 267$_{456}$	0056$_{3}$	0006 258^{253}
·001	0000 004$_{14}$	0000^{0}	0000 002^{8}	·051	0011 723$_{465}$	0059$_{2}$	0006 511^{258}
·002	0000 018$_{23}$	0000^{0}	0000 010^{12}	·052	0012 188$_{474}$	0061$_{2}$	0006 769^{263}
·003	0000 041$_{31}$	0000^{0}	0000 022^{18}	·053	0012 662$_{483}$	0063$_{2}$	0007 032^{269}
·004	0000 072$_{41}$	0000$^{0}_{1}$	0000 040^{22}	·054	0013 145$_{492}$	0066$_{2}$	0007 301^{273}
0·005	0000 113$_{49}$	0001	0000 062^{28}	0·055	0013 637$_{501}$	0068$_{3}$	0007 574^{278}
·006	0000 162$_{59}$	0001^{0}	0000 090^{32}	·056	0014 138$_{511}$	0071$_{3}$	0007 852^{284}
·007	0000 221$_{67}$	0001^{0}	0000 122^{38}	·057	0014 649$_{519}$	0073$_{2}$	0008 136^{288}
·008	0000 288$_{77}$	0001^{0}	0000 160^{43}	·058	0015 168$_{529}$	0076$_{3}$	0008 424^{294}
·009	0000 365$_{85}$	0002$^{0}_{0}$	0000 203^{47}	·059	0015 697$_{538}$	0079$_{2}$	0008 718^{298}
0·010	0000 450$_{95}$	0002	0000 250^{53}	0·060	0016 235$_{547}$	0081$_{3}$	0009 016^{304}
·011	0000 545$_{103}$	0003^{1}	0000 303^{57}	·061	0016 782$_{556}$	0084$_{3}$	0009 320^{309}
·012	0000 648$_{113}$	0003^{1}	0000 360^{63}	·062	0017 338$_{565}$	0087$_{3}$	0009 629^{313}
·013	0000 761$_{121}$	0004^{1}	0000 423^{67}	·063	0017 903$_{574}$	0090$_{2}$	0009 942^{319}
·014	0000 882$_{131}$	0004$^{1}_{0}$	0000 490^{73}	·064	0018 477$_{583}$	0092$_{3}$	0010 261^{324}
0·015	0001 013$_{139}$	0005^{1}	0000 563^{77}	0·065	0019 060$_{593}$	0095$_{3}$	0010 585^{329}
·016	0001 152$_{149}$	0006^{0}	0000 640^{83}	·066	0019 653$_{602}$	0098$_{3}$	0010 914^{334}
·017	0001 301$_{157}$	0006^{0}	0000 723^{87}	·067	0020 255$_{610}$	0101$_{3}$	0011 248^{339}
·018	0001 458$_{167}$	0007^{1}	0000 810^{93}	·068	0020 865$_{620}$	0104$_{3}$	0011 587^{344}
·019	0001 625$_{175}$	0008^{1}	0000 903^{97}	·069	0021 485$_{630}$	0108$_{4}$	0011 931^{349}
0·020	0001 800$_{185}$	0009^{1}	0001 000^{103}	0·070	0022 115$_{638}$	0111$_{3}$	0012 280^{354}
·021	0001 985$_{194}$	0010^{1}	0001 103^{107}	·071	0022 753$_{647}$	0114$_{3}$	0012 634^{360}
·022	0002 179$_{202}$	0011^{1}	0001 210^{113}	·072	0023 400$_{657}$	0117$_{3}$	0012 994^{364}
·023	0002 381$_{212}$	0012^{1}	0001 323^{117}	·073	0024 057$_{666}$	0120$_{3}$	0013 358^{370}
·024	0002 593$_{221}$	0013^{1}	0001 440^{123}	·074	0024 723$_{675}$	0124$_{3}$	0013 728^{374}
0·025	0002 814$_{229}$	0014^{1}	0001 563^{128}	0·075	0025 398$_{684}$	0127$_{4}$	0014 102^{380}
·026	0003 043$_{239}$	0015^{1}	0001 691^{132}	·076	0026 082$_{693}$	0131$_{4}$	0014 482^{385}
·027	0003 282$_{248}$	0016^{2}	0001 823^{138}	·077	0026 775$_{703}$	0134$_{3}$	0014 867^{389}
·028	0003 530$_{256}$	0018^{1}	0001 961^{142}	·078	0027 478$_{711}$	0138$_{3}$	0015 256^{395}
·029	0003 786$_{266}$	0019^{1}	0002 103^{148}	·079	0028 189$_{721}$	0141$_{4}$	0015 651^{400}
0·030	0004 052$_{275}$	0020^{2}	0002 251^{153}	0·080	0028 910$_{730}$	0145$_{3}$	0016 051^{406}
·031	0004 327$_{284}$	0022^{1}	0002 404^{157}	·081	0029 640$_{740}$	0148$_{4}$	0016 457^{410}
·032	0004 611$_{293}$	0023^{2}	0002 561^{163}	·082	0030 380$_{748}$	0152$_{4}$	0016 867^{415}
·033	0004 904$_{303}$	0025^{2}	0002 724^{168}	·083	0031 128$_{758}$	0156$_{4}$	0017 282^{421}
·034	0005 206$_{311}$	0026$^{1}_{2}$	0002 892^{172}	·084	0031 886$_{767}$	0160$_{4}$	0017 703^{425}
0·035	0005 517$_{319}$	0028	0003 064^{178}	0·085	0032 653$_{776}$	0164$_{3}$	0018 128^{431}
·036	0005 836$_{330}$	0029^{1}	0003 242^{183}	·086	0033 429$_{786}$	0167$_{4}$	0018 559^{435}
·037	0006 166$_{338}$	0031^{2}	0003 425^{188}	·087	0034 215$_{794}$	0171$_{4}$	0018 994^{441}
·038	0006 504$_{347}$	0033^{2}	0003 613^{192}	·088	0035 009$_{804}$	0175$_{4}$	0019 435^{446}
·039	0006 851$_{356}$	0034^{2}	0003 805^{198}	·089	0035 813$_{814}$	0179$_{4}$	0019 881^{451}
0·040	0007 207$_{365}$	0036^{2}	0004 003^{203}	0·090	0036 627$_{822}$	0183$_{5}$	0020 332^{457}
·041	0007 572$_{374}$	0038^{2}	0004 206^{208}	·091	0037 449$_{832}$	0188$_{4}$	0020 789^{461}
·042	0007 946$_{384}$	0040^{2}	0004 414^{213}	·092	0038 281$_{841}$	0192$_{4}$	0021 250^{467}
·043	0008 330$_{392}$	0042^{2}	0004 627^{218}	·093	0039 122$_{850}$	0196$_{4}$	0021 717^{471}
·044	0008 722$_{402}$	0044^{2}	0004 845^{223}	·094	0039 972$_{860}$	0200$_{5}$	0022 188^{477}
0·045	0009 124$_{410}$	0046^{2}	0005 068^{228}	0·095	0040 832$_{869}$	0205$_{4}$	0022 665^{482}
·046	0009 534$_{420}$	0048^{2}	0005 296^{233}	·096	0041 701$_{878}$	0209$_{4}$	0023 147^{487}
·047	0009 954$_{428}$	0050^{2}	0005 529^{238}	·097	0042 579$_{888}$	0213$_{5}$	0023 634^{492}
·048	0010 382$_{438}$	0052^{2}	0005 767^{243}	·098	0043 467$_{897}$	0218$_{5}$	0024 126^{497}
·049	0010 820$_{447}$	0054^{2}	0006 010^{248}	·099	0044 364$_{906}$	0222$_{5}$	0024 623^{503}
0·050	0011 267	0056	0006 258	0·100	0045 270	0227	0025 126

TABLE 1.

$\varepsilon^{\frac{1}{2}}\mu$	A	I	N	$\varepsilon^{\frac{1}{2}}\mu$	A	I	N
	1·	3·	1·		1·	3·	1·
0·100	0045 270$_{915}$	0227$_4$	0025 126$_{507}$	0·150	0102 627$_{1392}$	0516$_7$	0056 892$_{770}$
·101	0046 185$_{925}$	0231$_5$	0025 633$_{513}$	·151	0104 019$_{1402}$	0523$_7$	0057 662$_{775}$
·102	0047 110$_{934}$	0236$_5$	0026 146$_{518}$	·152	0105 421$_{1411}$	0530$_7$	0058 437$_{781}$
·103	0048 044$_{944}$	0241$_5$	0026 664$_{523}$	·153	0106 832$_{1421}$	0537$_7$	0059 218$_{786}$
·104	0048 988$_{953}$	0246$_4$	0027 187$_{529}$	·154	0108 253$_{1431}$	0544$_8$	0060 004$_{791}$
0·105	0049 941$_{962}$	0250$_5$	0027 716$_{533}$	0·155	0109 684$_{1441}$	0552$_7$	0060 795$_{797}$
·106	0050 903$_{971}$	0255$_5$	0028 249$_{539}$	·156	0111 125$_{1451}$	0559$_7$	0061 592$_{802}$
·107	0051 874$_{981}$	0260$_5$	0028 788$_{543}$	·157	0112 576$_{1460}$	0566$_8$	0062 394$_{807}$
·108	0052 855$_{991}$	0265$_5$	0029 331$_{549}$	·158	0114 036$_{1470}$	0574$_7$	0063 201$_{813}$
·109	0053 846$_{999}$	0270$_5$	0029 880$_{554}$	·159	0115 506$_{1481}$	0581$_8$	0064 014$_{819}$
0·110	0054 845$_{1010}$	0275$_5$	0030 434$_{560}$	0·160	0116 987$_{1490}$	0589$_7$	0064 833$_{823}$
·111	0055 855$_{1018}$	0280$_5$	0030 994$_{564}$	·161	0118 477$_{1499}$	0596$_8$	0065 656$_{829}$
·112	0056 873$_{1028}$	0285$_5$	0031 558$_{570}$	·162	0119 976$_{1510}$	0604$_7$	0066 485$_{835}$
·113	0057 901$_{1037}$	0290$_5$	0032 128$_{575}$	·163	0121 486$_{1520}$	0611$_8$	0067 320$_{840}$
·114	0058 938$_{1047}$	0296$_5$	0032 703$_{580}$	·164	0123 006$_{1529}$	0619$_8$	0068 160$_{845}$
0·115	0059 985$_{1056}$	0301$_5$	0033 283$_{585}$	0·165	0124 535$_{1540}$	0627$_8$	0069 005$_{851}$
·116	0061 041$_{1066}$	0306$_5$	0033 868$_{591}$	·166	0126 075$_{1549}$	0635$_7$	0069 856$_{856}$
·117	0062 107$_{1075}$	0312$_6$	0034 459$_{595}$	·167	0127 624$_{1560}$	0642$_8$	0070 712$_{862}$
·118	0063 182$_{1085}$	0317$_5$	0035 054$_{601}$	·168	0129 184$_{1569}$	0650$_8$	0071 574$_{867}$
·119	0064 267$_{1094}$	0322$_6$	0035 655$_{607}$	·169	0130 753$_{1579}$	0658$_8$	0072 441$_{872}$
0·120	0065 361$_{1103}$	0328$_6$	0036 262$_{611}$	0·170	0132 332$_{1589}$	0666$_8$	0073 313$_{878}$
·121	0066 464$_{1113}$	0334$_5$	0036 873$_{617}$	·171	0133 921$_{1600}$	0674$_8$	0074 191$_{884}$
·122	0067 577$_{1123}$	0339$_6$	0037 490$_{621}$	·172	0135 521$_{1609}$	0682$_9$	0075 075$_{889}$
·123	0068 700$_{1132}$	0345$_5$	0038 111$_{627}$	·173	0137 130$_{1619}$	0691$_8$	0075 964$_{894}$
·124	0069 832$_{1141}$	0350$_6$	0038 738$_{633}$	·174	0138 749$_{1629}$	0699$_8$	0076 858$_{900}$
0·125	0070 973$_{1152}$	0356$_6$	0039 371$_{637}$	0·175	0140 378$_{1640}$	0707$_8$	0077 758$_{905}$
·126	0072 125$_{1160}$	0362$_6$	0040 008$_{643}$	·176	0142 018$_{1649}$	0715$_9$	0078 663$_{911}$
·127	0073 285$_{1170}$	0368$_6$	0040 651$_{648}$	·177	0143 667$_{1659}$	0724$_8$	0079 574$_{916}$
·128	0074 455$_{1180}$	0374$_6$	0041 299$_{653}$	·178	0145 326$_{1670}$	0732$_9$	0080 490$_{922}$
·129	0075 635$_{1189}$	0380$_6$	0041 952$_{659}$	·179	0146 996$_{1679}$	0741$_8$	0081 412$_{927}$
0·130	0076 824$_{1199}$	0386$_6$	0042 611$_{664}$	0·180	0148 675$_{1690}$	0749$_9$	0082 339$_{933}$
·131	0078 023$_{1208}$	0392$_6$	0043 275$_{669}$	·181	0150 365$_{1700}$	0758$_8$	0083 272$_{939}$
·132	0079 231$_{1218}$	0398$_6$	0043 944$_{674}$	·182	0152 065$_{1710}$	0766$_9$	0084 211$_{943}$
·133	0080 449$_{1227}$	0404$_6$	0044 618$_{680}$	·183	0153 775$_{1720}$	0775$_9$	0085 154$_{950}$
·134	0081 676$_{1237}$	0410$_6$	0045 298$_{684}$	·184	0155 495$_{1730}$	0784$_9$	0086 104$_{955}$
0·135	0082 913$_{1247}$	0416$_7$	0045 982$_{691}$	0·185	0157 225$_{1740}$	0793$_9$	0087 059$_{960}$
·136	0084 160$_{1256}$	0423$_7$	0046 673$_{695}$	·186	0158 965$_{1751}$	0802$_8$	0088 019$_{966}$
·137	0085 416$_{1266}$	0429$_6$	0047 368$_{701}$	·187	0160 716$_{1761}$	0810$_9$	0088 985$_{972}$
·138	0086 682$_{1276}$	0435$_7$	0048 069$_{706}$	·188	0162 477$_{1771}$	0819$_9$	0089 957$_{977}$
·139	0087 958$_{1285}$	0442$_6$	0048 775$_{711}$	·189	0164 248$_{1781}$	0828$_9$	0090 934$_{983}$
0·140	0089 243$_{1295}$	0448$_7$	0049 486$_{717}$	0·190	0166 029$_{1791}$	0837$_{10}$	0091 917$_{988}$
·141	0090 538$_{1304}$	0455$_7$	0050 203$_{722}$	·191	0167 820$_{1802}$	0847$_9$	0092 905$_{994}$
·142	0091 842$_{1314}$	0461$_7$	0050 925$_{727}$	·192	0169 622$_{1812}$	0856$_9$	0093 899$_{999}$
·143	0093 156$_{1324}$	0468$_7$	0051 652$_{733}$	·193	0171 434$_{1822}$	0865$_9$	0094 898$_{1005}$
·144	0094 480$_{1334}$	0475$_7$	0052 385$_{737}$	·194	0173 256$_{1833}$	0874$_{10}$	0095 903$_{1011}$
0·145	0095 814$_{1343}$	0482$_6$	0053 122$_{744}$	0·195	0175 089$_{1842}$	0884$_9$	0096 914$_{1016}$
·146	0097 157$_{1353}$	0488$_7$	0053 866$_{748}$	·196	0176 931$_{1853}$	0893$_9$	0097 930$_{1022}$
·147	0098 510$_{1363}$	0495$_7$	0054 614$_{754}$	·197	0178 784$_{1864}$	0902$_{10}$	0098 952$_{1028}$
·148	0099 873$_{1372}$	0502$_7$	0055 368$_{759}$	·198	0180 648$_{1874}$	0912$_{10}$	0099 980$_{1033}$
·149	0101 245$_{1382}$	0509$_7$	0056 127$_{765}$	·199	0182 522$_{·1884}$	0921$_{10}$	0101 013$_{1038}$
0·150	0102 627	0516	0056 892	0·200	0184 406	0931	0102 051

TABLE 1.

$\varepsilon^{\frac{1}{2}}\mu$	A (1·)	I (3·)	N (1·)
0·200	$0184\ 406_{1894}$	0931_{10}	$0102\ 051^{1045}$
·201	$0186\ 300_{1905}$	0941_{10}	$0103\ 096^{1050}$
·202	$0188\ 205_{1916}$	0950_{9}	$0104\ 146^{1056}$
·203	$0190\ 121_{1926}$	0960_{10}	$0105\ 202^{1061}$
·204	$0192\ 047_{1936}$	0970_{10}	$0106\ 263^{1067}$
0·205	$0193\ 983_{1946}$	0980_{10}	$0107\ 330^{1073}$
·206	$0195\ 929_{1958}$	0990_{10}	$0108\ 403^{1078}$
·207	$0197\ 887_{1967}$	1000_{10}	$0109\ 481^{1084}$
·208	$0199\ 854_{1978}$	1010_{10}	$0110\ 565^{1090}$
·209	$0201\ 832_{1989}$	1020_{10}	$0111\ 655^{1095}$
0·210	$0203\ 821_{1999}$	1030_{10}	$0112\ 750^{1101}$
·211	$0205\ 820_{2010}$	1040_{11}	$0113\ 851^{1107}$
·212	$0207\ 830_{2020}$	1051_{10}	$0114\ 958^{1113}$
·213	$0209\ 850_{2031}$	1061_{10}	$0116\ 071^{1118}$
·214	$0211\ 881_{2041}$	1071_{11}	$0117\ 189^{1124}$
0·215	$0213\ 922_{2052}$	1082_{10}	$0118\ 313^{1130}$
·216	$0215\ 974_{2063}$	1092_{11}	$0119\ 443^{1136}$
·217	$0218\ 037_{2073}$	1103_{10}	$0120\ 579^{1141}$
·218	$0220\ 110_{2084}$	1113_{11}	$0121\ 720^{1147}$
·219	$0222\ 194_{2095}$	1124_{11}	$0122\ 867^{1153}$
0·220	$0224\ 289_{2105}$	1135_{11}	$0124\ 020^{1159}$
·221	$0226\ 394_{2116}$	1146_{10}	$0125\ 179^{1164}$
·222	$0228\ 510_{2127}$	1156_{11}	$0126\ 343^{1170}$
·223	$0230\ 637_{2138}$	1167_{11}	$0127\ 513^{1176}$
·224	$0232\ 775_{2148}$	1178_{11}	$0128\ 689^{1182}$
0·225	$0234\ 923_{2159}$	1189_{11}	$0129\ 871^{1188}$
·226	$0237\ 082_{2170}$	1200_{12}	$0131\ 059^{1193}$
·227	$0239\ 252_{2181}$	1212_{11}	$0132\ 252^{1200}$
·228	$0241\ 433_{2191}$	1223_{11}	$0133\ 452^{1205}$
·229	$0243\ 624_{2203}$	1234_{11}	$0134\ 657^{1211}$
0·230	$0245\ 827_{2213}$	1245_{12}	$0135\ 868^{1217}$
·231	$0248\ 040_{2224}$	1257_{11}	$0137\ 085^{1223}$
·232	$0250\ 264_{2235}$	1268_{12}	$0138\ 308^{1229}$
·233	$0252\ 499_{2246}$	1280_{11}	$0139\ 537^{1234}$
·234	$0254\ 745_{2257}$	1291_{12}	$0140\ 771^{1241}$
0·235	$0257\ 002_{2268}$	1303_{11}	$0142\ 012^{1246}$
·236	$0259\ 270_{2278}$	1314_{12}	$0143\ 258^{1252}$
·237	$0261\ 548_{2290}$	1326_{12}	$0144\ 510^{1259}$
·238	$0263\ 838_{2301}$	1338_{12}	$0145\ 769^{1264}$
·239	$0266\ 139_{2312}$	1350_{12}	$0147\ 033^{1270}$
0·240	$0268\ 451_{2323}$	1362_{11}	$0148\ 303^{1276}$
·241	$0270\ 774_{2334}$	1373_{12}	$0149\ 579^{1282}$
·242	$0273\ 108_{2345}$	1385_{13}	$0150\ 861^{1288}$
·243	$0275\ 453_{2356}$	1398_{12}	$0152\ 149^{1294}$
·244	$0277\ 809_{2367}$	1410_{12}	$0153\ 443^{1300}$
0·245	$0280\ 176_{2378}$	1422_{12}	$0154\ 743^{1306}$
·246	$0282\ 554_{2390}$	1434_{12}	$0156\ 049^{1311}$
·247	$0284\ 944_{2401}$	1446_{13}	$0157\ 360^{1318}$
·248	$0287\ 345_{2412}$	1459_{12}	$0158\ 678^{1324}$
·249	$0289\ 757_{2423}$	1471_{13}	$0160\ 002^{1330}$
0·250	$0292\ 180$	1484	$0161\ 332$
0·250	$0292\ 180_{2434}$	1484_{12}	$0161\ 332^{1336}$
·251	$0294\ 614_{2446}$	1496_{13}	$0162\ 668^{1342}$
·252	$0297\ 060_{2457}$	1509_{13}	$0164\ 010^{1348}$
·253	$0299\ 517_{2468}$	1522_{12}	$0165\ 358^{1355}$
·254	$0301\ 985_{2480}$	1534_{13}	$0166\ 713^{1360}$
0·255	$0304\ 465_{2491}$	1547_{13}	$0168\ 073^{1366}$
·256	$0306\ 956_{2502}$	1560_{13}	$0169\ 439^{1373}$
·257	$0309\ 458_{2514}$	1573_{13}	$0170\ 812^{1378}$
·258	$0311\ 972_{2525}$	1586_{13}	$0172\ 190^{1385}$
·259	$0314\ 497_{2536}$	1599_{13}	$0173\ 575^{1391}$
0·260	$0317\ 033_{2548}$	1612_{13}	$0174\ 966^{1396}$
·261	$0319\ 581_{2560}$	1625_{13}	$0176\ 362^{1404}$
·262	$0322\ 141_{2570}$	1638_{14}	$0177\ 766^{1409}$
·263	$0324\ 711_{2583}$	1652_{14}	$0179\ 175^{1415}$
·264	$0327\ 294_{2594}$	1665_{13}	$0180\ 590^{1422}$
0·265	$0329\ 888_{2605}$	1679_{13}	$0182\ 012^{1427}$
·266	$0332\ 493_{2617}$	1692_{14}	$0183\ 439^{1434}$
·267	$0335\ 110_{2629}$	1706_{13}	$0184\ 873^{1440}$
·268	$0337\ 739_{2640}$	1719_{14}	$0186\ 313^{1447}$
·269	$0340\ 379_{2652}$	1733_{14}	$0187\ 760^{1452}$
0·270	$0343\ 031_{2664}$	1747_{14}	$0189\ 212^{1459}$
·271	$0345\ 695_{2675}$	1761_{13}	$0190\ 671^{1465}$
·272	$0348\ 370_{2687}$	1774_{14}	$0192\ 136^{1471}$
·273	$0351\ 057_{2699}$	1788_{14}	$0193\ 607^{1478}$
·274	$0353\ 756_{2711}$	1802_{14}	$0195\ 085^{1483}$
0·275	$0356\ 467_{2722}$	1816_{15}	$0196\ 568^{1490}$
·276	$0359\ 189_{2734}$	1831_{14}	$0198\ 058^{1497}$
·277	$0361\ 923_{2746}$	1845_{14}	$0199\ 555^{1502}$
·278	$0364\ 669_{2758}$	1859_{14}	$0201\ 057^{1509}$
·279	$0367\ 427_{2769}$	1873_{15}	$0202\ 566^{1516}$
0·280	$0370\ 196_{2782}$	1888_{14}	$0204\ 082^{1521}$
·281	$0372\ 978_{2793}$	1902_{15}	$0205\ 603^{1528}$
·282	$0375\ 771_{2806}$	1917_{14}	$0207\ 131^{1535}$
·283	$0378\ 577_{2817}$	1931_{15}	$0208\ 666^{1540}$
·284	$0381\ 394_{2830}$	1946_{15}	$0210\ 206^{1547}$
0·285	$0384\ 224_{2841}$	1961_{15}	$0211\ 753^{1554}$
·286	$0387\ 065_{2853}$	1976_{14}	$0213\ 307^{1560}$
·287	$0389\ 918_{2866}$	1990_{15}	$0214\ 867^{1566}$
·288	$0392\ 784_{2878}$	2005_{15}	$0216\ 433^{1573}$
·289	$0395\ 662_{2889}$	2020_{15}	$0218\ 006^{1579}$
0·290	$0398\ 551_{2902}$	2035_{16}	$0219\ 585^{1586}$
·291	$0401\ 453_{2914}$	2051_{15}	$0221\ 171^{1592}$
·292	$0404\ 367_{2926}$	2066_{15}	$0222\ 763^{1598}$
·293	$0407\ 293_{2939}$	2081_{15}	$0224\ 361^{1605}$
·294	$0410\ 232_{2950}$	2096_{16}	$0225\ 966^{1612}$
0·295	$0413\ 182_{2963}$	2112_{15}	$0227\ 578^{1618}$
·296	$0416\ 145_{2975}$	2127_{16}	$0229\ 196^{1624}$
·297	$0419\ 120_{2988}$	2143_{15}	$0230\ 820^{1631}$
·298	$0422\ 108_{3000}$	2158_{16}	$0232\ 451^{1638}$
·299	$0425\ 108_{3012}$	2174_{16}	$0234\ 089^{1644}$
0·300	$0428\ 120$	2190	$0235\ 733$

TABLE 1.

$\varepsilon^{\frac{1}{2}}\mu$	A	I	N	$\varepsilon^{\frac{1}{2}}\mu$	A	I	N
	1·	3·	1·		1·	3·	1·
0·300	$0428\ 120_{3025}$	2190_{16}	$0235\ 733_{1651}$	0·350	$0595\ 130_{3682}$	3072_{19}	$0326\ 580_{1995}$
·301	$0431\ 145_{3037}$	2206_{16}	$0237\ 384_{1657}$	·351	$0598\ 812_{3696}$	3091_{20}	$0328\ 575_{2004}$
·302	$0434\ 182_{3049}$	2222_{16}	$0239\ 041_{1664}$	·352	$0602\ 508_{3709}$	3111_{20}	$0330\ 579_{2010}$
·303	$0437\ 231_{3062}$	2238_{16}	$0240\ 705_{1670}$	·353	$0606\ 217_{3724}$	3131_{19}	$0332\ 589_{2018}$
·304	$0440\ 293_{3075}$	2254_{16}	$0242\ 375_{1678}$	·354	$0609\ 941_{3738}$	3150_{20}	$0334\ 607_{2025}$
0·305	$0443\ 368_{3087}$	2270_{16}	$0244\ 053_{1683}$	0·355	$0613\ 679_{3751}$	3170_{20}	$0336\ 632_{2032}$
·306	$0446\ 455_{3099}$	2286_{16}	$0245\ 736_{1691}$	·356	$0617\ 430_{3766}$	3190_{21}	$0338\ 664_{2040}$
·307	$0449\ 554_{3113}$	2302_{16}	$0247\ 427_{1697}$	·357	$0621\ 196_{3780}$	3211_{20}	$0340\ 704_{2047}$
·308	$0452\ 667_{3124}$	2318_{16}	$0249\ 124_{1703}$	·358	$0624\ 976_{3794}$	3231_{20}	$0342\ 751_{2054}$
·309	$0455\ 791_{3138}$	2335_{17}	$0250\ 827_{1711}$	·359	$0628\ 770_{3809}$	3251_{20}	$0344\ 805_{2062}$
0·310	$0458\ 929_{3150}$	2351_{17}	$0252\ 538_{1717}$	0·360	$0632\ 579_{3823}$	3271_{21}	$0346\ 867_{2069}$
·311	$0462\ 079_{3163}$	2368_{16}	$0254\ 255_{1723}$	·361	$0636\ 402_{3837}$	3292_{20}	$0348\ 936_{2077}$
·312	$0465\ 242_{3175}$	2384_{17}	$0255\ 978_{1731}$	·362	$0640\ 239_{3851}$	3312_{21}	$0351\ 013_{2084}$
·313	$0468\ 417_{3188}$	2401_{17}	$0257\ 709_{1737}$	·363	$0644\ 090_{3866}$	3333_{21}	$0353\ 097_{2091}$
·314	$0471\ 605_{3202}$	2418_{17}	$0259\ 446_{1744}$	·364	$0647\ 956_{3880}$	3354_{20}	$0355\ 188_{2099}$
0·315	$0474\ 807_{3213}$	2435_{17}	$0261\ 190_{1751}$	0·365	$0651\ 836_{3895}$	3374_{21}	$0357\ 287_{2107}$
·316	$0478\ 020_{3227}$	2452_{17}	$0262\ 941_{1757}$	·366	$0655\ 731_{3909}$	3395_{21}	$0359\ 394_{2114}$
·317	$0481\ 247_{3240}$	2469_{17}	$0264\ 698_{1764}$	·367	$0659\ 640_{3924}$	3416_{21}	$0361\ 508_{2122}$
·318	$0484\ 487_{3252}$	2486_{17}	$0266\ 462_{1771}$	·368	$0663\ 564_{3939}$	3437_{21}	$0363\ 630_{2137}$
·319	$0487\ 739_{3266}$	2503_{17}	$0268\ 233_{1778}$	·369	$0667\ 503_{3953}$	3458_{22}	$0365\ 759_{2137}$
0·320	$0491\ 005_{3278}$	2520_{17}	$0270\ 011_{1785}$	0·370	$0671\ 456_{3967}$	3480_{21}	$0367\ 896_{2144}$
·321	$0494\ 283_{3291}$	2537_{17}	$0271\ 796_{1791}$	·371	$0675\ 423_{3983}$	3501_{21}	$0370\ 040_{2152}$
·322	$0497\ 574_{3305}$	2555_{18}	$0273\ 587_{1799}$	·372	$0679\ 406_{3997}$	3522_{22}	$0372\ 192_{2160}$
·323	$0500\ 879_{3317}$	2572_{17}	$0275\ 386_{1805}$	·373	$0683\ 403_{4012}$	3544_{21}	$0374\ 352_{2167}$
·324	$0504\ 196_{3331}$	2590_{17}	$0277\ 191_{1812}$	·374	$0687\ 415_{4026}$	3565_{22}	$0376\ 519_{2175}$
0·325	$0507\ 527_{3343}$	2607_{18}	$0279\ 003_{1819}$	0·375	$0691\ 441_{4042}$	3587_{22}	$0378\ 694_{2182}$
·326	$0510\ 870_{3357}$	2625_{17}	$0280\ 822_{1826}$	·376	$0695\ 483_{4056}$	3609_{22}	$0380\ 876_{2190}$
·327	$0514\ 227_{3370}$	2642_{18}	$0282\ 648_{1832}$	·377	$0699\ 539_{4071}$	3631_{22}	$0383\ 066_{2198}$
·328	$0517\ 597_{3383}$	2660_{18}	$0284\ 480_{1840}$	·378	$0703\ 610_{4087}$	3653_{22}	$0385\ 264_{2206}$
·329	$0520\ 980_{3396}$	2678_{18}	$0286\ 320_{1847}$	·379	$0707\ 697_{4101}$	3675_{22}	$0387\ 470_{2213}$
0·330	$0524\ 376_{3410}$	2696_{18}	$0288\ 167_{1853}$	0·380	$0711\ 798_{4117}$	3697_{22}	$0389\ 683_{2222}$
·331	$0527\ 786_{3423}$	2714_{18}	$0290\ 020_{1861}$	·381	$0715\ 915_{4131}$	3719_{22}	$0391\ 905_{2228}$
·332	$0531\ 209_{3436}$	2732_{18}	$0291\ 881_{1867}$	·382	$0720\ 046_{4147}$	3741_{22}	$0394\ 133_{2237}$
·333	$0534\ 645_{3450}$	2750_{19}	$0293\ 748_{1875}$	·383	$0724\ 193_{4162}$	3764_{23}	$0396\ 370_{2245}$
·334	$0538\ 095_{3462}$	2769_{18}	$0295\ 623_{1882}$	·384	$0728\ 355_{4177}$	3786_{22}	$0398\ 615_{2252}$
0·335	$0541\ 557_{3477}$	2787_{18}	$0297\ 505_{1888}$	0·385	$0732\ 532_{4192}$	3809_{23}	$0400\ 867_{2261}$
·336	$0545\ 034_{3490}$	2805_{19}	$0299\ 393_{1896}$	·386	$0736\ 724_{4207}$	3831_{22}	$0403\ 128_{2268}$
·337	$0548\ 524_{3503}$	2824_{18}	$0301\ 289_{1902}$	·387	$0740\ 931_{4223}$	3854_{23}	$0405\ 396_{2276}$
·338	$0552\ 027_{3517}$	2842_{19}	$0303\ 191_{1910}$	·388	$0745\ 154_{4239}$	3877_{23}	$0407\ 672_{2284}$
·339	$0555\ 544_{3530}$	2861_{19}	$0305\ 101_{1917}$	·389	$0749\ 393_{4254}$	3900_{23}	$0409\ 956_{2292}$
0·340	$0559\ 074_{3544}$	2880_{19}	$0307\ 018_{1924}$	0·390	$0753\ 647_{4269}$	3923_{23}	$0412\ 248_{2300}$
·341	$0562\ 618_{3558}$	2899_{19}	$0308\ 942_{1931}$	·391	$0757\ 916_{4285}$	3946_{23}	$0414\ 548_{2307}$
·342	$0566\ 176_{3571}$	2918_{19}	$0310\ 873_{1938}$	·392	$0762\ 201_{4300}$	3969_{24}	$0416\ 855_{2316}$
·343	$0569\ 747_{3585}$	2937_{19}	$0312\ 811_{1946}$	·393	$0766\ 501_{4316}$	3993_{23}	$0419\ 171_{2324}$
·344	$0573\ 332_{3598}$	2956_{19}	$0314\ 757_{1952}$	·394	$0770\ 817_{4332}$	4016_{23}	$0421\ 495_{2332}$
0·345	$0576\ 930_{3613}$	2975_{19}	$0316\ 709_{1960}$	0·395	$0775\ 149_{4347}$	4040_{23}	$0423\ 827_{2340}$
·346	$0580\ 543_{3626}$	2994_{19}	$0318\ 669_{1967}$	·396	$0779\ 496_{4363}$	4063_{24}	$0426\ 167_{2348}$
·347	$0584\ 169_{3640}$	3013_{20}	$0320\ 636_{1974}$	·397	$0783\ 859_{4379}$	4087_{24}	$0428\ 515_{2356}$
·348	$0587\ 809_{3654}$	3033_{19}	$0322\ 610_{1981}$	·398	$0788\ 238_{4395}$	4111_{24}	$0430\ 871_{2364}$
·349	$0591\ 463_{3667}$	3052_{20}	$0324\ 591_{1989}$	·399	$0792\ 633_{4410}$	4135_{24}	$0433\ 235_{2373}$
0·350	0595 130	3072	0326 580	0·400	0797 043	4159	0435 608

TABLE 1.

$\varepsilon^{\frac12}\mu$	A	I	N	$\varepsilon^{\frac12}\mu$	A	I	N
	1·	3·	1·		1·	3·	1·
0·400	0797 043$_{4427}$	4159$_{24}$	0435 608$_{2380}$	0·450	1038 906$_{5288}$	5492$_{29}$	0565 081$_{2817}$
·401	0801 470$_{4442}$	4183$_{24}$	0437 988$_{2389}$	·451	1044 194$_{5306}$	5521$_{30}$	0567 898$_{2826}$
·402	0805 912$_{4459}$	4207$_{24}$	0440 377$_{2397}$	·452	1049 500$_{5325}$	5551$_{30}$	0570 724$_{2836}$
·403	0810 371$_{4474}$	4231$_{25}$	0442 774$_{2405}$	·453	1054 825$_{5343}$	5581$_{30}$	0573 560$_{2845}$
·404	0814 845$_{4491}$	4256$_{24}$	0445 179$_{2413}$	·454	1060 168$_{5362}$	5611$_{30}$	0576 405$_{2855}$
0·405	0819 336$_{4507}$	4280$_{25}$	0447 592$_{2422}$	0·455	1065 530$_{5382}$	5641$_{30}$	0579 260$_{2864}$
·406	0823 843$_{4523}$	4305$_{25}$	0450 014$_{2430}$	·456	1070 912$_{5400}$	5671$_{30}$	0582 124$_{2873}$
·407	0828 366$_{4539}$	4329$_{25}$	0452 444$_{2438}$	·457	1076 312$_{5419}$	5701$_{30}$	0584 997$_{2883}$
·408	0832 905$_{4556}$	4354$_{25}$	0454 882$_{2446}$	·458	1081 731$_{5438}$	5732$_{31}$	0587 880$_{2893}$
·409	0837 461$_{4572}$	4379$_{25}$	0457 328$_{2455}$	·459	1087 169$_{5458}$	5762$_{30}$	0590 773$_{2902}$
0·410	0842 033$_{4588}$	4404$_{25}$	0459 783$_{2463}$	0·460	1092 627$_{5476}$	5793$_{30}$	0593 675$_{2912}$
·411	0846 621$_{4605}$	4429$_{25}$	0462 246$_{2472}$	·461	1098 103$_{5496}$	5823$_{31}$	0596 587$_{2922}$
·412	0851 226$_{4621}$	4454$_{26}$	0464 718$_{2480}$	·462	1103 599$_{5516}$	5854$_{31}$	0599 509$_{2931}$
·413	0855 847$_{4638}$	4480$_{25}$	0467 198$_{2488}$	·463	1109 115$_{5534}$	5885$_{32}$	0602 440$_{2941}$
·414	0860 485$_{4654}$	4505$_{25}$	0469 686$_{2497}$	·464	1114 649$_{5554}$	5917$_{31}$	0605 381$_{2950}$
0·415	0865 139$_{4671}$	4530$_{26}$	0472 183$_{2506}$	0·465	1120 203$_{5574}$	5948$_{31}$	0608 331$_{2960}$
·416	0869 810$_{4688}$	4556$_{26}$	0474 689$_{2514}$	·466	1125 777$_{5593}$	5979$_{31}$	0611 291$_{2971}$
·417	0874 498$_{4705}$	4582$_{26}$	0477 203$_{2522}$	·467	1131 370$_{5613}$	6011$_{32}$	0614 262$_{2979}$
·418	0879 203$_{4721}$	4608$_{26}$	0479 725$_{2531}$	·468	1136 983$_{5633}$	6042$_{31}$	0617 241$_{2990}$
·419	0883 924$_{4738}$	4634$_{26}$	0482 256$_{2539}$	·469	1142 616$_{5652}$	6074$_{32}$	0620 231$_{3000}$
0·420	0888 662$_{4755}$	4660$_{26}$	0484 795$_{2549}$	0·470	1148 268$_{5673}$	6106$_{32}$	0623 231$_{3009}$
·421	0893 417$_{4772}$	4686$_{26}$	0487 344$_{2556}$	·471	1153 941$_{5692}$	6138$_{32}$	0626 240$_{3020}$
·422	0898 189$_{4789}$	4712$_{26}$	0489 900$_{2566}$	·472	1159 633$_{5713}$	6170$_{33}$	0629 260$_{3029}$
·423	0902 978$_{4806}$	4738$_{27}$	0492 466$_{2574}$	·473	1165 346$_{5732}$	6203$_{32}$	0632 289$_{3040}$
·424	0907 784$_{4824}$	4765$_{26}$	0495 040$_{2582}$	·474	1171 078$_{5753}$	6235$_{33}$	0635 329$_{3049}$
0·425	0912 608$_{4840}$	4791$_{27}$	0497 622$_{2592}$	0·475	1176 831$_{5773}$	6268$_{33}$	0638 378$_{3060}$
·426	0917 448$_{4857}$	4818$_{27}$	0500 214$_{2600}$	·476	1182 604$_{5793}$	6301$_{32}$	0641 438$_{3069}$
·427	0922 305$_{4875}$	4845$_{27}$	0502 814$_{2609}$	·477	1188 397$_{5813}$	6333$_{33}$	0644 507$_{3080}$
·428	0927 180$_{4892}$	4872$_{27}$	0505 423$_{2617}$	·478	1194 210$_{5834}$	6366$_{34}$	0647 587$_{3090}$
·429	0932 072$_{4910}$	4899$_{27}$	0508 040$_{2627}$	·479	1200 044$_{5855}$	6400$_{33}$	0650 677$_{3100}$
0·430	0936 982$_{4927}$	4926$_{27}$	0510 667$_{2635}$	0·480	1205 899$_{5875}$	6433$_{33}$	0653 777$_{3110}$
·431	0941 909$_{4944}$	4953$_{27}$	0513 302$_{2644}$	·481	1211 774$_{5895}$	6466$_{34}$	0656 887$_{3121}$
·432	0946 853$_{4962}$	4980$_{28}$	0515 946$_{2653}$	·482	1217 669$_{5917}$	6500$_{33}$	0660 008$_{3131}$
·433	0951 815$_{4980}$	5008$_{28}$	0518 599$_{2662}$	·483	1223 586$_{5937}$	6533$_{34}$	0663 139$_{3131}$
·434	0956 795$_{4997}$	5035$_{27}$	0521 261$_{2671}$	·484	1229 523$_{5958}$	6567$_{34}$	0666 280$_{3141}$
0·435	0961 792$_{5015}$	5063$_{28}$	0523 932$_{2679}$	0·485	1235 481$_{5979}$	6601$_{34}$	0669 431$_{3162}$
·436	0966 807$_{5032}$	5091$_{28}$	0526 611$_{2689}$	·486	1241 460$_{6001}$	6635$_{34}$	0672 593$_{3172}$
·437	0971 839$_{5051}$	5119$_{28}$	0529 300$_{2698}$	·487	1247 461$_{6021}$	6670$_{35}$	0675 765$_{3183}$
·438	0976 890$_{5068}$	5147$_{28}$	0531 998$_{2706}$	·488	1253 482$_{6042}$	6704$_{34}$	0678 948$_{3193}$
·439	0981 958$_{5087}$	5175$_{28}$	0534 704$_{2716}$	·489	1259 524$_{6064}$	6739$_{34}$	0682 141$_{3204}$
0·440	0987 045$_{5104}$	5203$_{28}$	0537 420$_{2725}$	0·490	1265 588$_{6085}$	6773$_{35}$	0685 345$_{3214}$
·441	0992 149$_{5122}$	5231$_{29}$	0540 145$_{2734}$	·491	1271 673$_{6107}$	6808$_{35}$	0688 559$_{3225}$
·442	0997 271$_{5141}$	5260$_{29}$	0542 879$_{2743}$	·492	1277 780$_{6128}$	6843$_{35}$	0691 784$_{3236}$
·443	1002 412$_{5158}$	5288$_{29}$	0545 622$_{2752}$	·493	1283 908$_{6149}$	6878$_{35}$	0695 020$_{3246}$
·444	1007 570$_{5177}$	5317$_{29}$	0548 374$_{2762}$	·494	1290 057$_{6171}$	6913$_{36}$	0698 266$_{3256}$
0·445	1012 747$_{5195}$	5346$_{29}$	0551 136$_{2770}$	0·495	1296 228$_{6193}$	6949$_{35}$	0701 522$_{3268}$
·446	1017 942$_{5213}$	5375$_{29}$	0553 906$_{2780}$	·496	1302 421$_{6215}$	6984$_{35}$	0704 790$_{3278}$
·447	1023 155$_{5232}$	5404$_{29}$	0556 686$_{2789}$	·497	1308 636$_{6237}$	7020$_{36}$	0708 068$_{3289}$
·448	1028 387$_{5251}$	5433$_{29}$	0559 475$_{2798}$	·498	1314 873$_{6259}$	7056$_{36}$	0711 357$_{3300}$
·449	1033 638$_{5268}$	5462$_{30}$	0562 273$_{2808}$	·499	1321 132$_{6280}$	7092$_{36}$	0714 657$_{3311}$
0·450	1038 906	5492	0565 081	0·500	1327 412	7128	0717 968

TABLE 1.

$\varepsilon^{\frac{3}{2}}\mu$	A (1.)	I (3.)	N (1.)
0·500	$1327\ 412_{6303}$	7128_{36}	$0717\ 968_{3321}$
·501	$1333\ 715_{6325}$	7164_{37}	$0721\ 289_{3333}$
·502	$1340\ 040_{6348}$	7201_{37}	$0724\ 622_{3343}$
·503	$1346\ 388_{6369}$	7238_{36}	$0727\ 965_{3355}$
·504	$1352\ 757_{6393}$	7274_{37}	$0731\ 320_{3365}$
0·505	$1359\ 150_{6415}$	7311_{37}	$0734\ 685_{3377}$
·506	$1365\ 565_{6437}$	7348_{38}	$0738\ 062_{3388}$
·507	$1372\ 002_{6460}$	7386_{37}	$0741\ 450_{3399}$
·508	$1378\ 462_{6483}$	7423_{37}	$0744\ 849_{3410}$
·509	$1384\ 945_{6506}$	7461_{38}	$0748\ 259_{3421}$
0·510	$1391\ 451_{6529}$	7498_{38}	$0751\ 680_{3433}$
·511	$1397\ 980_{6552}$	7536_{38}	$0755\ 113_{3444}$
·512	$1404\ 532_{6576}$	7574_{38}	$0758\ 557_{3455}$
·513	$1411\ 108_{6598}$	7612_{38}	$0762\ 012_{3466}$
·514	$1417\ 706_{6622}$	7651_{39}	$0765\ 478_{3478}$
0·515	$1424\ 328_{6645}$	7689_{39}	$0768\ 956_{3490}$
·516	$1430\ 973_{6669}$	7728_{39}	$0772\ 446_{3501}$
·517	$1437\ 642_{6693}$	7767_{39}	$0775\ 947_{3512}$
·518	$1444\ 335_{6716}$	7806_{39}	$0779\ 459_{3524}$
·519	$1451\ 051_{6740}$	7845_{39}	$0782\ 983_{3536}$
0·520	$1457\ 791_{6764}$	7884_{40}	$0786\ 519_{3548}$
·521	$1464\ 555_{6788}$	7924_{40}	$0790\ 067_{3559}$
·522	$1471\ 343_{6812}$	7964_{39}	$0793\ 626_{3571}$
·523	$1478\ 155_{6836}$	8003_{40}	$0797\ 197_{3582}$
·524	$1484\ 991_{6860}$	8043_{41}	$0800\ 779_{3595}$
0·525	$1491\ 851_{6885}$	8084_{40}	$0804\ 374_{3606}$
·526	$1498\ 736_{6909}$	8124_{41}	$0807\ 980_{3618}$
·527	$1505\ 645_{6934}$	8165_{40}	$0811\ 598_{3630}$
·528	$1512\ 579_{6959}$	8205_{41}	$0815\ 228_{3642}$
·529	$1519\ 538_{6983}$	8246_{41}	$0818\ 870_{3655}$
0·530	$1526\ 521_{7009}$	8287_{42}	$0822\ 525_{3666}$
·531	$1533\ 530_{7033}$	8329_{41}	$0826\ 191_{3678}$
·532	$1540\ 563_{7058}$	8370_{42}	$0829\ 869_{3691}$
·533	$1547\ 621_{7084}$	8412_{41}	$0833\ 560_{3703}$
·534	$1554\ 705_{7108}$	8453_{42}	$0837\ 263_{3715}$
0·535	$1561\ 813_{7135}$	8495_{43}	$0840\ 978_{3727}$
·536	$1568\ 948_{7159}$	8538_{42}	$0844\ 705_{3740}$
·537	$1576\ 107_{7186}$	8580_{42}	$0848\ 445_{3752}$
·538	$1583\ 293_{7210}$	8622_{43}	$0852\ 197_{3764}$
·539	$1590\ 503_{7237}$	8665_{43}	$0855\ 961_{3777}$
0·540	$1597\ 740_{7263}$	8708_{43}	$0859\ 738_{3790}$
·541	$1605\ 003_{7289}$	8751_{43}	$0863\ 528_{3802}$
·542	$1612\ 292_{7314}$	8794_{44}	$0867\ 330_{3815}$
·543	$1619\ 606_{7341}$	8838_{44}	$0871\ 145_{3827}$
·544	$1626\ 947_{7368}$	8882_{43}	$0874\ 972_{3840}$
0·545	$1634\ 315_{7394}$	8925_{44}	$0878\ 812_{3853}$
·546	$1641\ 709_{7420}$	8969_{45}	$0882\ 665_{3865}$
·547	$1649\ 129_{7447}$	9014_{44}	$0886\ 530_{3879}$
·548	$1656\ 576_{7474}$	9058_{45}	$0890\ 409_{3891}$
·549	$1664\ 050_{7501}$	9103_{45}	$0894\ 300_{3905}$
0·550	$1671\ 551$	9148	$0898\ 205$

$\varepsilon^{\frac{3}{2}}\mu$	A (1.)	I	N (1.)
0·550	$1671\ 551_{7528}$	$3 \cdot 9148_{45}$	$0898\ 205_{3917}$
·551	$1679\ 079_{7555}$	9193_{45}	$0902\ 122_{3930}$
·552	$1686\ 634_{7582}$	9238_{45}	$0906\ 052_{3944}$
·553	$1694\ 216_{7609}$	9283_{45}	$0909\ 996_{3957}$
·554	$1701\ 825_{7637}$	9329_{46}	$0913\ 953_{3969}$
0·555	$1709\ 462_{7665}$	$3 \cdot 9375_{46}$	$0917\ 922_{3984}$
·556	$1717\ 127_{7692}$	9421_{46}	$0921\ 906_{3996}$
·557	$1724\ 819_{7721}$	9467_{46}	$0925\ 902_{4010}$
·558	$1732\ 540_{7748}$	9513_{46}	$0929\ 912_{4023}$
·559	$1740\ 288_{7776}$	9560_{47}	$0933\ 935_{4036}$
0·560	$1748\ 064_{7804}$	$3 \cdot 9607_{47}$	$0937\ 971_{4051}$
·561	$1755\ 868_{7833}$	9654_{47}	$0942\ 022_{4063}$
·562	$1763\ 701_{7861}$	9701_{47}	$0946\ 085_{4078}$
·563	$1771\ 562_{7890}$	9749_{48}	$0950\ 163_{4091}$
·564	$1779\ 452_{7919}$	9796_{47}	$0954\ 254_{4104}$
0·565	$1787\ 371_{7947}$	$3 \cdot 9844_{48}$	$0958\ 358_{4119}$
·566	$1795\ 318_{7976}$	9892_{48}	$0962\ 477_{4132}$
·567	$1803\ 294_{8006}$	9941_{49}	$0966\ 609_{4146}$
·568	$1811\ 300_{8034}$	$3 \cdot 9989_{48}$	$0970\ 755_{4160}$
·569	$1819\ 334_{8064}$	$4 \cdot 0038_{49}$	$0974\ 915_{4174}$
0·570	$1827\ 398_{8093}$	$4 \cdot 0087_{49}$	$0979\ 089_{4189}$
·571	$1835\ 491_{8123}$	0136_{49}	$0983\ 278_{4202}$
·572	$1843\ 614_{8153}$	0186_{49}	$0987\ 480_{4216}$
·573	$1851\ 767_{8183}$	0235_{50}	$0991\ 696_{4231}$
·574	$1859\ 950_{8212}$	0285_{50}	$0995\ 927_{4245}$
0·575	$1868\ 162_{8243}$	$4 \cdot 0335_{51}$	$1000\ 172_{4259}$
·576	$1876\ 405_{8273}$	0386_{50}	$1004\ 431_{4274}$
·577	$1884\ 678_{8303}$	0436_{50}	$1008\ 705_{4288}$
·578	$1892\ 981_{8334}$	0487_{51}	$1012\ 993_{4303}$
·579	$1901\ 315_{8365}$	0538_{51}	$1017\ 296_{4317}$
0·580	$1909\ 680_{8395}$	$4 \cdot 0589_{52}$	$1021\ 613_{4332}$
·581	$1918\ 075_{8427}$	0641_{52}	$1025\ 945_{4346}$
·582	$1926\ 502_{8457}$	0693_{52}	$1030\ 291_{4361}$
·583	$1934\ 959_{8489}$	0745_{52}	$1034\ 652_{4376}$
·584	$1943\ 448_{8520}$	0797_{52}	$1039\ 028_{4391}$
0·585	$1951\ 968_{8552}$	$4 \cdot 0849_{53}$	$1043\ 419_{4406}$
·586	$1960\ 520_{8583}$	0902_{53}	$1047\ 825_{4421}$
·587	$1969\ 103_{8616}$	0955_{53}	$1052\ 246_{4436}$
·588	$1977\ 719_{8647}$	1008_{54}	$1056\ 682_{4451}$
·589	$1986\ 366_{8679}$	1062_{54}	$1061\ 133_{4466}$
0·590	$1995\ 045_{8712}$	$4 \cdot 1116_{53}$	$1065\ 599_{4482}$
·591	$2003\ 757_{8744}$	1169_{55}	$1070\ 081_{4497}$
·592	$2012\ 501_{8777}$	1224_{55}	$1074\ 578_{4512}$
·593	$2021\ 278_{8810}$	1278_{54}	$1079\ 090_{4527}$
·594	$2030\ 088_{8842}$	1333_{55}	$1083\ 617_{4543}$
0·595	$2038\ 930_{8876}$	$4 \cdot 1388_{55}$	$1088\ 160_{4559}$
·596	$2047\ 806_{8908}$	1443_{55}	$1092\ 719_{4575}$
·597	$2056\ 714_{8942}$	1499_{56}	$1097\ 294_{4590}$
·598	$2065\ 656_{8976}$	1554_{55}	$1101\ 884_{4605}$
·599	$2074\ 632_{.9009}$	1610_{56}	$1106\ 489_{4622}$
0·600	$2083\ 641$	$4 \cdot 1667$	$1111\ 111$

TABLE 2.

ε	c	h	ε	c	h
0·000	1·000 0000 ^{4001}	0·00000 ^{100}	**0·050**	0·979 7508 ^{4102}	0·05149 ^{107}
·001	0·999 5999 ^{4003}	·00100 ^{100}	·051	·979 3406 ^{4104}	·05256 ^{106}
·002	·999 1996 ^{4005}	·00200 ^{100}	·052	·978 9302 ^{4106}	·05362 ^{106}
·003	·998 7991 ^{4007}	·00301 ^{101}	·053	·978 5196 ^{4108}	·05468 ^{107}
·004	·998 3984 ^{4008}	·00401 ^{100}	·054	·978 1088 ^{4111}	·05575 ^{106}
0·005	0·997 9976 ^{4011}	0·00501 ^{101}	**0·055**	0·977 6977 ^{4112}	0·05681 ^{107}
·006	·997 5965 ^{4013}	·00602 ^{101}	·056	·977 2865 ^{4115}	·05788 ^{107}
·007	·997 1952 ^{4014}	·00703 ^{101}	·057	·976 8750 ^{4117}	·05895 ^{107}
·008	·996 7938 ^{4017}	·00804 ^{101}	·058	·976 4633 ^{4119}	·06002 ^{107}
·009	·996 3921 ^{4019}	·00905 ^{101}	·059	·976 0514 ^{4121}	·06109 ^{108}
0·010	0·995 9902 ^{4020}	0·01006 ^{101}	**0·060**	0·975 6393 ^{4123}	0·06217 ^{107}
·011	·995 5882 ^{4023}	·01107 ^{101}	·061	·975 2270 ^{4125}	·06324 ^{108}
·012	·995 1859 ^{4024}	·01208 ^{102}	·062	·974 8145 ^{4128}	·06432 ^{107}
·013	·994 7835 ^{4027}	·01310 ^{101}	·063	·974 4017 ^{4129}	·06539 ^{108}
·014	·994 3808 ^{4028}	·01411 ^{102}	·064	·973 9888 ^{4132}	·06647 ^{108}
0·015	0·993 9780 ^{4031}	0·01513 ^{102}	**0·065**	0·973 5756 ^{4134}	0·06755 ^{108}
·016	·993 5749 ^{4032}	·01615 ^{102}	·066	·973 1622 ^{4136}	·06863 ^{108}
·017	·993 1717 ^{4035}	·01717 ^{102}	·067	·972 7486 ^{4138}	·06971 ^{109}
·018	·992 7682 ^{4036}	·01820 ^{103}	·068	·972 3348 ^{4141}	·07080 ^{108}
·019	·992 3646 ^{4039}	·01921 ^{101}	·069	·971 9207 ^{4142}	·07188 ^{109}
0·020	0·991 9607 ^{4040}	0·02023 ^{103}	**0·070**	0·971 5065 ^{4145}	0·07297 ^{108}
·021	·991 5567 ^{4042}	·02126 ^{103}	·071	·971 0920 ^{4147}	·07405 ^{109}
·022	·991 1525 ^{4045}	·02228 ^{102}	·072	·970 6773 ^{4149}	·07514 ^{109}
·023	·990 7480 ^{4046}	·02331 ^{103}	·073	·970 2624 ^{4151}	·07623 ^{109}
·024	·990 3434 ^{4049}	·02434 ^{103}	·074	·969 8473 ^{4153}	·07732 ^{110}
0·025	0·989 9385 ^{4050}	0·02537 ^{103}	**0·075**	0·969 4320 ^{4156}	0·07842 ^{109}
·026	·989 5335 ^{4053}	·02640 ^{103}	·076	·969 0164 ^{4158}	·07951 ^{110}
·027	·989 1282 ^{4054}	·02743 ^{103}	·077	·968 6006 ^{4160}	·08061 ^{109}
·028	·988 7228 ^{4057}	·02846 ^{104}	·078	·968 1846 ^{4162}	·08170 ^{110}
·029	·988 3171 ^{4059}	·02950 ^{103}	·079	·967 7684 ^{4164}	·08280 ^{110}
0·030	0·987 9112 ^{4060}	0·03053 ^{104}	**0·080**	0·967 3520 ^{4167}	0·08390 ^{110}
·031	·987 5052 ^{4063}	·03157 ^{103}	·081	·966 9353 ^{4169}	·08500 ^{110}
·032	·987 0989 ^{4065}	·03260 ^{104}	·082	·966 5184 ^{4171}	·08610 ^{111}
·033	·986 6924 ^{4067}	·03364 ^{104}	·083	·966 1013 ^{4173}	·08721 ^{110}
·034	·986 2857 ^{4068}	·03468 ^{104}	·084	·965 6840 ^{4175}	·08831 ^{111}
0·035	0·985 8789 ^{4071}	0·03572 ^{105}	**0·085**	0·965 2665 ^{4178}	0·08942 ^{110}
·036	·985 4718 ^{4073}	·03677 ^{104}	·086	·964 8487 ^{4180}	·09052 ^{111}
·037	·985 0645 ^{4075}	·03781 ^{105}	·087	·964 4307 ^{4182}	·09163 ^{111}
·038	·984 6570 ^{4077}	·03886 ^{104}	·088	·964 0125 ^{4184}	·09274 ^{111}
·039	·984 2493 ^{4079}	·03990 ^{105}	·089	·963 5941 ^{4187}	·09385 ^{112}
0·040	0·983 8414 ^{4081}	0·04095 ^{105}	**0·090**	0·963 1754 ^{4188}	0·09497 ^{111}
·041	·983 4333 ^{4084}	·04200 ^{105}	·091	·962 7566 ^{4192}	·09608 ^{112}
·042	·983 0249 ^{4085}	·04305 ^{105}	·092	·962 3374 ^{4193}	·09720 ^{111}
·043	·982 6164 ^{4087}	·04410 ^{105}	·093	·961 9181 ^{4195}	·09831 ^{112}
·044	·982 2077 ^{4090}	·04515 ^{106}	·094	·961 4986 ^{4198}	·09943 ^{112}
0·045	0·981 7987 ^{4091}	0·04621 ^{105}	**0·095**	0·961 0788 ^{4200}	0·10055 ^{112}
·046	·981 3896 ^{4094}	·04726 ^{106}	·096	·960 6588 ^{4203}	·10167 ^{112}
·047	·980 9802 ^{4096}	·04832 ^{105}	·097	·960 2385 ^{4204}	·10279 ^{113}
·048	·980 5706 ^{4098}	·04937 ^{106}	·098	·959 8181 ^{4207}	·10392 ^{112}
·049	·980 1608 ^{4100}	·05043 ^{106}	·099	·959 3974 ^{4209}	·10504 ^{113}
0·050	0·979 7508	0·05149	**0·100**	0·958 9765	0·10617

TABLE 3.

$\varepsilon^{\frac{1}{2}}\sigma$	J	K	$\varepsilon^{\frac{1}{2}}\sigma$	J	K
0·000	1·000 0000	0·000 0000	**0·050**	0·999 6250	0·000 0071$_3$
·001	0·999 9998 $_2$	0000^0	·051	·999 6099^{151}	0074$_3^3$
·002	·999 9994 $_4$	0000^0	·052	·999 5944^{155}	0077$_3^3$
·003	·999 9986 $_8$	0000^0	·053	·999 5787^{157}	0080$_3^3$
·004	·999 9976 $_{10}^{14}$	0000$_1^0$	·054	·999 5626$^{161}_{163}$	0083$_3^3$
0·005	0·999 9962	0·000 0001$_1$	**0·055**	0·999 5463	0·000 0086$_3$
·006	·999 9946 $_{16}$	0001^0	·056	·999 5296^{167}	0089$_3^3$
·007	·999 9926 $_{20}$	0001^0	·057	·999 5127^{169}	0093$_3^4$
·008	·999 9904 $_{22}$	0002^0	·058	·999 4954^{173}	0096$_3^3$
·009	·999 9878 $_{26}^{28}$	0002$_1^0$	·059	·999 4779$^{175}_{179}$	0099$_4^3$
0·010	0·999 9850	0·000 0003$_0$	**0·060**	0·999 4600	0·000 0103$_3$
·011	·999 9818 $_{32}$	0003^0	·061	·999 4419^{181}	0106$_3^3$
·012	·999 9784 $_{34}$	0004^1	·062	·999 4234^{185}	0110$_4^4$
·013	·999 9746 $_{38}$	0005^1	·063	·999 4047^{187}	0113$_3^3$
·014	·999 9706 $_{40}^{44}$	0006$_0^1$	·064	·999 3856$^{191}_{193}$	0117$_4^4$
0·015	0·999 9662	0·000 0006$_1$	**0·065**	0·999 3663	0·000 0121$_3$
·016	·999 9616 $_{46}$	0007^1	·066	·999 3466^{197}	0124$_3^3$
·017	·999 9566 $_{50}$	0008^1	·067	·999 3267^{199}	0128$_4^4$
·018	·999 9514 $_{52}$	0009^1	·068	·999 3064^{203}	0132$_4^4$
·019	·999 9458 $_{56}^{58}$	0010$_1^1$	·069	·999 2859$^{205}_{209}$	0136$_4^4$
0·020	0·999 9400	0·000 0011$_2$	**0·070**	0·999 2650	0·000 0140$_4$
·021	·999 9338 $_{62}$	0013^1	·071	·999 2439^{211}	0144$_4^4$
·022	·999 9274 $_{64}$	0014^1	·072	·999 2224^{215}	0148$_4^4$
·023	·999 9206 $_{68}$	0015^1	·073	·999 2007^{217}	0152$_4^4$
·024	·999 9136 $_{70}^{74}$	0016$_2^1$	·074	·999 1786$^{221}_{223}$	0156$_4^4$
0·025	0·999 9062	0·000 0018$_1$	**0·075**	0·999 1563	0·000 0160$_5$
·026	·999 8986 $_{76}$	0019^1	·076	·999 1336^{227}	0165$_4^5$
·027	·999 8907 $_{79}$	0021^2	·077	·999 1107^{229}	0169$_4^4$
·028	·999 8824 $_{83}$	0022^1	·078	·999 0874^{233}	0173$_4^4$
·029	·999 8739 $_{85}^{89}$	0024$_2^2$	·079	·999 0639$^{235}_{239}$	0178$_4^5$
0·030	0·999 8650	0·000 0026$_1$	**0·080**	0·999 0400	0·000 0182$_5$
·031	·999 8559 $_{91}$	0027^1	·081	·999 0159^{241}	0187$_5^5$
·032	·999 8464 $_{95}$	0029^2	·082	·998 9914^{245}	0192$_5^5$
·033	·999 8367 $_{97}$	0031^2	·083	·998 9667^{247}	0196$_4^5$
·034	·999 8266 $_{101}^{103}$	0033$_2^2$	·084	·998 9416$^{251}_{253}$	0201$_5^5$
0·035	0·999 8163	0·000 0035$_2$	**0·085**	0·998 9163	0·000 0206$_5$
·036	·999 8056^{107}	0037^2	·086	·998 8906^{257}	0211$_5^5$
·037	·999 7947^{109}	0039^2	·087	·998 8647^{259}	0216$_5^5$
·038	·999 7834^{113}	0041^2	·088	·998 8384^{263}	0221$_5^5$
·039	·999 7719$^{115}_{119}$	0043$_3^2$	·089	·998 8119$^{265}_{269}$	0226$_5^5$
0·040	0·999 7600	0·000 0046$_2$	**0·090**	0·998 7850	0·000 0231$_5$
·041	·999 7479^{121}	0048^2	·091	·998 7579^{271}	0236$_5^5$
·042	·999 7354^{125}	0050^2	·092	·998 7305^{274}	0241$_5^5$
·043	·999 7227^{127}	0053^3	·093	·998 7027^{278}	0246$_5^5$
·044	·999 7096$^{131}_{133}$	0055$_3^2$	·094	·998 6747$^{280}_{284}$	0252$_5^6$
0·045	0·999 6963	0·000 0058$_2$	**0·095**	0·998 6463	0·000 0257$_5$
·046	·999 6826^{137}	0060^2	·096	·998 6177^{286}	0262$_6^5$
·047	·999 6687^{139}	0063^3	·097	·998 5887^{290}	0268$_5^6$
·048	·999 6544^{143}	0066^3	·098	·998 5595^{292}	0273$_6^5$
·049	·999 6399$^{145}_{149}$	0069$_2^3$	·099	·998 5299$^{296}_{298}$	0279$_6^6$
0·050	0·999 6250	0·000 0071	**0·100**	0·998 5001	0·000 0285

TABLE 3.

$\varepsilon^{\frac{1}{2}}\sigma$	J	K	$\varepsilon^{\frac{1}{2}}\sigma$	J	K
0·100	0·998 5001$_{302}$	0·000 0285$_5$	0·150	0·996 6254$_{452}$	0·000 0637$_9$
·101	·998 4699$_{304}$	0290$_5$	·151	·996 5802$_{454}$	0646$_8$
·102	·998 4395$_{308}$	0296$_6$	·152	·996 5348$_{458}$	0654$_9$
·103	·998 4087$_{310}$	0302$_6$	·153	·996 4890$_{460}$	0663$_8$
·104	·998 3777$_{314}$	0308$_6$	·154	·996 4430$_{463}$	0671$_9$
0·105	0·998 3463$_{316}$	0·000 0314$_6$	0·155	0·996 3967$_{467}$	0·000 0680$_9$
·106	·998 3147$_{320}$	0320$_6$	·156	·996 3500$_{469}$	0689$_8$
·107	·998 2827$_{322}$	0326$_6$	·157	·996 3031$_{473}$	0697$_9$
·108	·998 2505$_{325}$	0332$_6$	·158	·996 2558$_{475}$	0706$_9$
·109	·998 2180$_{329}$	0338$_6$	·159	·996 2083$_{478}$	0715$_9$
0·110	0·998 1851$_{331}$	0·000 0344$_6$	0·160	0·996 1605$_{482}$	0·000 0724$_9$
·111	·998 1520$_{335}$	0350$_7$	·161	·996 1123$_{484}$	0733$_9$
·112	·998 1185$_{337}$	0357$_6$	·162	·996 0639$_{487}$	0742$_9$
·113	·998 0848$_{341}$	0363$_6$	·163	·996 0152$_{491}$	0751$_9$
·114	·998 0507$_{343}$	0369$_7$	·164	·995 9661$_{493}$	0760$_9$
0·115	0·998 0164$_{347}$	0·000 0376$_6$	0·165	0·995 9168$_{497}$	0·000 0769$_{10}$
·116	·997 9817$_{349}$	0382$_7$	·166	·995 8671$_{499}$	0779$_9$
·117	·997 9468$_{353}$	0389$_7$	·167	·995 8172$_{502}$	0788$_9$
·118	·997 9115$_{355}$	0396$_6$	·168	·995 7670$_{506}$	0797$_{10}$
·119	·997 8760$_{359}$	0402$_7$	·169	·995 7164$_{508}$	0807$_9$
0·120	0·997 8401$_{361}$	0·000 0409$_7$	0·170	0·995 6656$_{511}$	0·000 0816$_{10}$
·121	·997 8040$_{364}$	0416$_7$	·171	·995 6145$_{515}$	0826$_9$
·122	·997 7676$_{368}$	0423$_7$	·172	·995 5630$_{517}$	0835$_{10}$
·123	·997 7308$_{370}$	0430$_7$	·173	·995 5113$_{520}$	0845$_{10}$
·124	·997 6938$_{374}$	0437$_7$	·174	·995 4593$_{524}$	0855$_9$
0·125	0·997 6564$_{376}$	0·000 0444$_7$	0·175	0·995 4069$_{526}$	0·000 0864$_{10}$
·126	·997 6188$_{380}$	0451$_7$	·176	·995 3543$_{529}$	0874$_{10}$
·127	·997 5808$_{382}$	0458$_7$	·177	·995 3014$_{533}$	0884$_{10}$
·128	·997 5426$_{386}$	0465$_7$	·178	·995 2481$_{535}$	0894$_{10}$
·129	·997 5040$_{388}$	0472$_8$	·179	·995 1946$_{538}$	0904$_{10}$
0·130	0·997 4652$_{391}$	0·000 0480$_7$	0·180	0·995 1408$_{542}$	0·000 0914$_{10}$
·131	·997 4261$_{395}$	0487$_7$	·181	·995 0866$_{544}$	0924$_{10}$
·132	·997 3866$_{397}$	0494$_7$	·182	·995 0322$_{547}$	0934$_{10}$
·133	·997 3469$_{401}$	0502$_7$	·183	·994 9775$_{551}$	0944$_{10}$
·134	·997 3068$_{403}$	0509$_8$	·184	·994 9224$_{553}$	0954$_{11}$
0·135	0·997 2665$_{407}$	0·000 0517$_8$	0·185	0·994 8671$_{556}$	0·000 0965$_{10}$
·136	·997 2258$_{409}$	0525$_7$	·186	·994 8115$_{560}$	0975$_{10}$
·137	·997 1849$_{412}$	0532$_7$	·187	·994 7555$_{562}$	0985$_{11}$
·138	·997 1437$_{416}$	0540$_8$	·188	·994 6993$_{565}$	0996$_{10}$
·139	·997 1021$_{418}$	0548$_8$	·189	·994 6428$_{569}$	1006$_{11}$
0·140	0·997 0603$_{422}$	0·000 0556$_8$	0·190	0·994 5859$_{571}$	0·000 1017$_{10}$
·141	·997 0181$_{424}$	0564$_8$	·191	·994 5288$_{574}$	1027$_{11}$
·142	·996 9757$_{428}$	0572$_8$	·192	·994 4714$_{578}$	1038$_{11}$
·143	·996 9329$_{430}$	0580$_8$	·193	·994 4136$_{580}$	1049$_{10}$
·144	·996 8899$_{433}$	0588$_8$	·194	·994 3556$_{583}$	1059$_{11}$
0·145	0·996 8466$_{437}$	0·000 0596$_8$	0·195	0·994 2973$_{586}$	0·000 1070$_{11}$
·146	·996 8029$_{439}$	0604$_8$	·196	·994 2387$_{590}$	1081$_{11}$
·147	·996 7590$_{443}$	0612$_8$	·197	·994 1797$_{592}$	1092$_{11}$
·148	·996 7147$_{445}$	0620$_8$	·198	·994 1205$_{595}$	1103$_{11}$
·149	·996 6702$_{448}$	0629$_8$	·199	·994 0610$_{599}$	1114$_{11}$
0·150	0·996 6254	0·000 0637	0·200	0·994 0011	0·000 1125

TABLE 3.

$\varepsilon^{\frac{1}{2}}\sigma$	J	K	$\varepsilon^{\frac{1}{2}}\sigma$	J	K
0·200	0·994 0011$_{601}$	0·000 1125$_{11}$	0·250	0·990 6278$_{751}$	0·000 1742$_{13}$
·201	·993 9410$_{604}$	1136$_{11}$	·251	·990 5527$_{754}$	1755$_{13}$
·202	·993 8806$_{607}$	1147$_{11}$	·252	·990 4773$_{757}$	1769$_{14}$
·203	·993 8199$_{611}$	1158$_{11}$	·253	·990 4016$_{760}$	1783$_{14}$
·204	·993 7588$_{613}$	1169$_{12}$	·254	·990 3256$_{763}$	1796$_{14}$
0·205	0·993 6975$_{616}$	0·000 1181$_{11}$	0·255	0·990 2493$_{766}$	0·000 1810$_{14}$
·206	·993 6359$_{619}$	1192$_{12}$	·256	·990 1727$_{769}$	1824$_{14}$
·207	·993 5740$_{623}$	1204$_{11}$	·257	·990 0958$_{772}$	1838$_{14}$
·208	·993 5117$_{625}$	1215$_{11}$	·258	·990 0186$_{775}$	1852$_{14}$
·209	·993 4492$_{628}$	1226$_{12}$	·259	·989 9411$_{778}$	1866$_{14}$
0·210	0·993 3864$_{631}$	0·000 1238$_{12}$	0·260	0·989 8633$_{781}$	0·000 1880$_{14}$
·211	·993 3233$_{635}$	1250$_{11}$	·261	·989 7852$_{784}$	1894$_{14}$
·212	·993 2598$_{637}$	1261$_{11}$	·262	·989 7068$_{787}$	1908$_{14}$
·213	·993 1961$_{640}$	1273$_{12}$	·263	·989 6281$_{790}$	1922$_{14}$
·214	·993 1321$_{643}$	1285$_{12}$	·264	·989 5491$_{793}$	1936$_{15}$
0·215	0·993 0678$_{646}$	0·000 1297$_{11}$	0·265	0·989 4698$_{796}$	0·000 1951$_{14}$
·216	·993 0032$_{650}$	1308$_{12}$	·266	·989 3902$_{799}$	1965$_{14}$
·217	·992 9382$_{652}$	1320$_{12}$	·267	·989 3103$_{802}$	1979$_{15}$
·218	·992 8730$_{655}$	1332$_{12}$	·268	·989 2301$_{805}$	1994$_{14}$
·219	·992 8075$_{658}$	1344$_{12}$	·269	·989 1496$_{808}$	2008$_{15}$
0·220	0·992 7417$_{661}$	0·000 1356$_{13}$	0·270	0·989 0688$_{811}$	0·000 2023$_{14}$
·221	·992 6756$_{665}$	1369$_{12}$	·271	·988 9877$_{814}$	2037$_{15}$
·222	·992 6091$_{667}$	1381$_{12}$	·272	·988 9063$_{817}$	2052$_{15}$
·223	·992 5424$_{670}$	1393$_{12}$	·273	·988 8246$_{820}$	2067$_{15}$
·224	·992 4754$_{673}$	1405$_{12}$	·274	·988 7426$_{822}$	2081$_{15}$
0·225	0·992 4081$_{676}$	0·000 1417$_{13}$	0·275	0·988 6604$_{826}$	0·000 2096$_{15}$
·226	·992 3405$_{679}$	1430$_{12}$	·276	·988 5778$_{829}$	2111$_{15}$
·227	·992 2726$_{683}$	1442$_{13}$	·277	·988 4949$_{832}$	2126$_{15}$
·228	·992 2043$_{685}$	1455$_{12}$	·278	·988 4117$_{835}$	2141$_{15}$
·229	·992 1358$_{688}$	1467$_{13}$	·279	·988 3282$_{838}$	2156$_{14}$
0·230	0·992 0670$_{691}$	0·000 1480$_{12}$	0·280	0·988 2444$_{841}$	0·000 2170$_{16}$
·231	·991 9979$_{694}$	1492$_{13}$	·281	·988 1603$_{844}$	2186$_{15}$
·232	·991 9285$_{697}$	1505$_{13}$	·282	·988 0759$_{846}$	2201$_{15}$
·233	·991 8588$_{701}$	1518$_{13}$	·283	·987 9913$_{850}$	2216$_{15}$
·234	·991 7887$_{703}$	1531$_{12}$	·284	·987 9063$_{853}$	2231$_{15}$
0·235	0·991 7184$_{706}$	0·000 1543$_{13}$	0·285	0·987 8210$_{856}$	0·000 2246$_{15}$
·236	·991 6478$_{709}$	1556$_{13}$	·286	·987 7354$_{859}$	2261$_{16}$
·237	·991 5769$_{712}$	1569$_{13}$	·287	·987 6495$_{862}$	2277$_{15}$
·238	·991 5057$_{715}$	1582$_{13}$	·288	·987 5633$_{864}$	2292$_{15}$
·239	·991 4342$_{718}$	1595$_{13}$	·289	·987 4769$_{868}$	2307$_{16}$
0·240	0·991 3624$_{721}$	0·000 1608$_{13}$	0·290	0·987 3901$_{871}$	0·000 2323$_{15}$
·241	·991 2903$_{724}$	1621$_{13}$	·291	·987 3030$_{874}$	2338$_{16}$
·242	·991 2179$_{728}$	1634$_{14}$	·292	·987 2156$_{877}$	2354$_{15}$
·243	·991 1451$_{730}$	1648$_{13}$	·293	·987 1279$_{879}$	2369$_{16}$
·244	·991 0721$_{733}$	1661$_{13}$	·294	·987 0400$_{883}$	2385$_{16}$
0·245	0·990 9988$_{736}$	0·000 1674$_{14}$	0·295	0·986 9517$_{886}$	0·000 2401$_{15}$
·246	·990 9252$_{739}$	1688$_{13}$	·296	·986 8631$_{889}$	2416$_{16}$
·247	·990 8513$_{742}$	1701$_{14}$	·297	·986 7742$_{891}$	2432$_{16}$
·248	·990 7771$_{745}$	1715$_{13}$	·298	·986 6851$_{895}$	2448$_{16}$
·249	·990 7026$_{748}$	1728$_{14}$	·299	·986 5956$_{898}$	2464$_{16}$
0·250	0·990 6278	0·000 1742	0·300	0·986 5058	0·000 2480

TABLE 3.

$\varepsilon^{\frac{1}{2}}\sigma$	J	K	$\varepsilon^{\frac{1}{2}}\sigma$	J	K
0·300	0·986 5058 $_{901}$	0·000 2480$_{16}$	**0·350**	0·981 6358 $_{1050}$	0·000 3330$_{18}$
·301	·986 4157 $_{903}$	2496$_{16}$	·351	·981 5308 $_{1054}$	3348$_{18}$
·302	·986 3254 $_{907}$	2512$_{16}$	·352	·981 4254 $_{1056}$	3366$_{18}$
·303	·986 2347 $_{910}$	2528$_{16}$	·353	·981 3198 $_{1059}$	3384$_{18}$
·304	·986 1437 $_{912}$	2544$_{16}$	·354	·981 2139 $_{1062}$	3402$_{19}$
0·305	0·986 0525 $_{916}$	0·000 2560$_{16}$	**0·355**	0·981 1077 $_{1065}$	0·000 3421$_{18}$
·306	·985 9609 $_{919}$	2576$_{16}$	·356	·981 0012 $_{1069}$	3439$_{18}$
·307	·985 8690 $_{921}$	2592$_{17}$	·357	·980 8943 $_{1071}$	3457$_{19}$
·308	·985 7769 $_{925}$	2609$_{16}$	·358	·980 7872 $_{1074}$	3476$_{18}$
·309	·985 6844 $_{928}$	2625$_{16}$	·359	·980 6798 $_{1077}$	3494$_{18}$
0·310	0·985 5916 $_{930}$	0·000 2641$_{17}$	**0·360**	0·980 5721 $_{1080}$	0·000 3512$_{19}$
·311	·985 4986 $_{934}$	2658$_{16}$	·361	·980 4641 $_{1083}$	3531$_{18}$
·312	·985 4052 $_{937}$	2674$_{16}$	·362	·980 3558 $_{1087}$	3549$_{19}$
·313	·985 3115 $_{939}$	2690$_{16}$	·363	·980 2471 $_{1089}$	3568$_{19}$
·314	·985 2176 $_{943}$	2707$_{17}$	·364	·980 1382 $_{1092}$	3587$_{18}$
0·315	0·985 1233 $_{945}$	0·000 2724$_{16}$	**0·365**	0·980 0290 $_{1095}$	0·000 3605$_{19}$
·316	·985 0288 $_{949}$	2740$_{17}$	·366	·979 9195 $_{1098}$	3624$_{19}$
·317	·984 9339 $_{952}$	2757$_{16}$	·367	·979 8097 $_{1101}$	3643$_{18}$
·318	·984 8387 $_{954}$	2773$_{17}$	·368	·979 6996 $_{1104}$	3661$_{19}$
·319	·984 7433 $_{958}$	2790$_{17}$	·369	·979 5892 $_{1107}$	3680$_{19}$
0·320	0·984 6475 $_{960}$	0·000 2807$_{17}$	**0·370**	0·979 4785 $_{1110}$	0·000 3699$_{19}$
·321	·984 5515 $_{964}$	2824$_{17}$	·371	·979 3675 $_{1113}$	3718$_{19}$
·322	·984 4551 $_{966}$	2841$_{17}$	·372	·979 2562 $_{1116}$	3737$_{19}$
·323	·984 3585 $_{970}$	2858$_{17}$	·373	·979 1446 $_{1119}$	3756$_{19}$
·324	·984 2615 $_{972}$	2875$_{17}$	·374	·979 0327 $_{1122}$	3775$_{19}$
0·325	0·984 1643 $_{976}$	0·000 2892$_{17}$	**0·375**	0·978 9205 $_{1125}$	0·000 3794$_{19}$
·326	·984 0667 $_{978}$	2909$_{17}$	·376	·978 8080 $_{1128}$	3813$_{19}$
·327	·983 9689 $_{982}$	2926$_{17}$	·377	·978 6952 $_{1131}$	3832$_{19}$
·328	·983 8707 $_{984}$	2943$_{17}$	·378	·978 5821 $_{1134}$	3851$_{19}$
·329	·983 7723 $_{988}$	2960$_{17}$	·379	·978 4687 $_{1137}$	3870$_{19}$
0·330	0·983 6735 $_{990}$	0·000 2977$_{17}$	**0·380**	0·978 3550 $_{1140}$	0·000 3889$_{19}$
·331	·983 5745 $_{994}$	2994$_{18}$	·381	·978 2410 $_{1143}$	3908$_{20}$
·332	·983 4751 $_{996}$	3012$_{17}$	·382	·978 1267 $_{1146}$	3928$_{19}$
·333	·983 3755 $_{1000}$	3029$_{17}$	·383	·978 0121 $_{1148}$	3947$_{19}$
·334	·983 2755 $_{1002}$	3046$_{18}$	·384	·977 8973 $_{1152}$	3966$_{20}$
0·335	0·983 1753 $_{1005}$	0·000 3064$_{17}$	**0·385**	0·977 7821 $_{1155}$	0·000 3986$_{19}$
·336	·983 0748 $_{1009}$	3081$_{18}$	·386	·977 6666 $_{1158}$	4005$_{20}$
·337	·982 9739 $_{1011}$	3099$_{17}$	·387	·977 5508 $_{1161}$	4025$_{19}$
·338	·982 8728 $_{1015}$	3116$_{18}$	·388	·977 4347 $_{1164}$	4044$_{20}$
·339	·982 7713 $_{1017}$	3134$_{17}$	·389	·977 3183 $_{1166}$	4064$_{19}$
0·340	0·982 6696 $_{1020}$	0·000 3151$_{18}$	**0·390**	0·977 2017 $_{1170}$	0·000 4083$_{20}$
·341	·982 5676 $_{1024}$	3169$_{18}$	·391	·977 0847 $_{1173}$	4103$_{19}$
·342	·982 4652 $_{1026}$	3187$_{18}$	·392	·976 9674 $_{1176}$	4122$_{20}$
·343	·982 3626 $_{1029}$	3205$_{17}$	·393	·976 8498 $_{1178}$	4142$_{20}$
·344	·982 2597 $_{1033}$	3222$_{18}$	·394	·976 7320 $_{1182}$	4162$_{20}$
0·345	0·982 1564 $_{1035}$	0·000 3240$_{18}$	**0·395**	0·976 6138 $_{1185}$	0·000 4182$_{19}$
·346	·982 0529 $_{1038}$	3258$_{18}$	·396	·976 4953 $_{1187}$	4201$_{20}$
·347	·981 9491 $_{1042}$	3276$_{18}$	·397	·976 3766 $_{1191}$	4221$_{20}$
·348	·981 8449 $_{1044}$	3294$_{18}$	·398	·976 2575 $_{1194}$	4241$_{20}$
·349	·981 7405 $_{1047}$	3312$_{18}$	·399	·976 1381 $_{1197}$	4261$_{20}$
0·350	0·981 6358	0·000 3330	**0·400**	0·976 0184	0·000 4281

TABLE 3.

$\varepsilon^{\frac{1}{2}}\sigma$	J	K	$\varepsilon^{\frac{1}{2}}\sigma$	J	K
0·400	0·976 0184$_{1199}$	0·000 4281$_{20}$	0·450	0·969 6546$_{1349}$	0·000 5319$_{22}$
·401	·975 8985$_{1203}$	4301$_{20}$	·451	·969 5197$_{1351}$	5341$_{22}$
·402	·975 7782$_{1205}$	4321$_{20}$	·452	·969 3846$_{1355}$	5362$_{21}$
·403	·975 6577$_{1209}$	4341$_{20}$	·453	·969 2491$_{1358}$	5384$_{22}$
·404	·975 5368$_{1212}$	4361$_{20}$	·454	·969 1133$_{1361}$	5406$_{21}$
0·405	0·975 4156$_{1214}$	0·000 4381$_{20}$	0·455	·968 9772$_{1364}$	0·000 5427$_{22}$
·406	·975 2942$_{1218}$	4401$_{20}$	·456	·968 8408$_{1366}$	5449$_{22}$
·407	·975 1724$_{1220}$	4421$_{20}$	·457	·968 7042$_{1370}$	5471$_{21}$
·408	·975 0504$_{1224}$	4441$_{21}$	·458	·968 5672$_{1373}$	5492$_{22}$
·409	·974 9280$_{1226}$	4462$_{20}$	·459	·968 4299$_{1375}$	5514$_{22}$
0·410	0·974 8054$_{1230}$	0·000 4482$_{20}$	0·460	·968 2924$_{1379}$	0·000 5536$_{22}$
·411	·974 6824$_{1232}$	4502$_{20}$	·461	·968 1545$_{1382}$	5558$_{22}$
·412	·974 5592$_{1236}$	4523$_{21}$	·462	·968 0163$_{1384}$	5580$_{22}$
·413	·974 4356$_{1238}$	4543$_{20}$	·463	·967 8779$_{1388}$	5602$_{22}$
·414	·974 3118$_{1242}$	4563$_{20}$	·464	·967 7391$_{1390}$	5624$_{22}$
0·415	0·974 1876$_{1244}$	0·000 4584$_{20}$	0·465	·967 6001$_{1394}$	0·000 5646$_{22}$
·416	·974 0632$_{1247}$	4604$_{21}$	·466	·967 4607$_{1397}$	5668$_{22}$
·417	·973 9385$_{1251}$	4625$_{20}$	·467	·967 3210$_{1399}$	5690$_{22}$
·418	·973 8134$_{1253}$	4645$_{21}$	·468	·967 1811$_{1403}$	5712$_{22}$
·419	·973 6881$_{1257}$	4666$_{20}$	·469	·967 0408$_{1405}$	5734$_{22}$
0·420	0·973 5624$_{1259}$	0·000 4686$_{21}$	0·470	·966 9003$_{1409}$	0·000 5756$_{22}$
·421	·973 4365$_{1262}$	4707$_{21}$	·471	·966 7594$_{1411}$	5778$_{22}$
·422	·973 3103$_{1266}$	4728$_{20}$	·472	·966 6183$_{1414}$	5800$_{22}$
·423	·973 1837$_{1268}$	4748$_{21}$	·473	·966 4769$_{1418}$	5822$_{22}$
·424	·973 0569$_{1271}$	4769$_{21}$	·474	·966 3351$_{1420}$	5844$_{23}$
0·425	0·972 9298$_{1274}$	0·000 4790$_{21}$	0·475	·966 1931$_{1424}$	0·000 5867$_{22}$
·426	·972 8024$_{1278}$	4811$_{21}$	·476	·966 0507$_{1426}$	5889$_{22}$
·427	·972 6746$_{1280}$	4832$_{20}$	·477	·965 9081$_{1429}$	5911$_{22}$
·428	·972 5466$_{1283}$	4852$_{21}$	·478	·965 7652$_{1433}$	5933$_{23}$
·429	·972 4183$_{1286}$	4873$_{21}$	·479	·965 6219$_{1435}$	5956$_{22}$
0·430	0·972 2897$_{1289}$	0·000 4894$_{21}$	0·480	·965 4784$_{1438}$	0·000 5978$_{22}$
·431	·972 1608$_{1293}$	4915$_{21}$	·481	·965 3346$_{1441}$	6000$_{22}$
·432	·972 0315$_{1295}$	4936$_{21}$	·482	·965 1905$_{1445}$	6023$_{22}$
·433	·971 9020$_{1298}$	4957$_{21}$	·483	·965 0460$_{1447}$	6045$_{22}$
·434	·971 7722$_{1301}$	4978$_{21}$	·484	·964 9013$_{1450}$	6068$_{22}$
0·435	0·971 6421$_{1304}$	0·000 4999$_{21}$	0·485	·964 7563$_{1453}$	0·000 6090$_{23}$
·436	·971 5117$_{1307}$	5020$_{22}$	·586	·964 6110$_{1456}$	6113$_{22}$
·437	·971 3810$_{1310}$	5042$_{21}$	·487	·964 4654$_{1459}$	6135$_{22}$
·438	·971 2500$_{1313}$	5063$_{21}$	·488	·964 3195$_{1463}$	6158$_{22}$
·439	·971 1187$_{1316}$	5084$_{21}$	·489	·964 1732$_{1465}$	6180$_{23}$
0·440	0·970 9871$_{1319}$	0·000 5105$_{21}$	0·490	·964 0267$_{1468}$	0·000 6203$_{23}$
·441	·970 8552$_{1322}$	5126$_{22}$	·491	·963 8799$_{1471}$	6226$_{22}$
·442	·970 7230$_{1325}$	5148$_{21}$	·492	·963 7328$_{1474}$	6248$_{23}$
·443	·970 5905$_{1328}$	5169$_{21}$	·493	·963 5854$_{1477}$	6271$_{22}$
·444	·970 4577$_{1331}$	5190$_{22}$	·494	·963 4377$_{1480}$	6293$_{23}$
0·445	0·970 3246$_{1334}$	0·000 5212$_{21}$	0·495	·963 2897$_{1483}$	0·000 6316$_{23}$
·446	·970 1912$_{1337}$	5233$_{22}$	·496	·963 1414$_{1486}$	6339$_{23}$
·447	·970 0575$_{1340}$	5255$_{21}$	·497	·962 9928$_{1489}$	6362$_{22}$
·448	·969 9235$_{1343}$	5276$_{22}$	·498	·962 8439$_{1491}$	6384$_{23}$
·449	·969 7892$_{1346}$	5298$_{21}$	·499	·962 6948$_{1493}$	6407$_{23}$
0·450	0·969 6546	0·000 5319	0·500	0·962 5453	0·000 6430

M

TABLE 3.

$\epsilon^{\frac{1}{2}}\sigma$	J	K	$\epsilon^{\frac{1}{2}}\sigma$	J	K
0·500	$0.962\ 5453_{1498}$	$0.000\ 6430_{23}$	**0·550**	$0.954\ 6915_{1647}$	$0.000\ 7596_{24}$
·501	$.962\ 3955_{1501}$	6453_{23}	·551	$.954\ 5268_{1649}$	7620_{24}
·502	$.962\ 2454_{1504}$	6476_{23}	·552	$.954\ 3619_{1653}$	7644_{24}
·503	$.962\ 0950_{1506}$	6499_{23}	·553	$.954\ 1966_{1655}$	7668_{24}
·504	$.961\ 9444_{1510}$	6522_{23}	·554	$.954\ 0311_{1659}$	7692_{23}
0·505	$0.961\ 7934_{1513}$	$0.000\ 6545_{22}$	**0·555**	$0.953\ 8652_{1661}$	$0.000\ 7715_{24}$
·506	$.961\ 6421_{1516}$	6567_{23}	·556	$.953\ 6991_{1665}$	7739_{24}
·507	$.961\ 4905_{1518}$	6590_{23}	·557	$.953\ 5326_{1667}$	7763_{24}
·508	$.961\ 3387_{1522}$	6613_{23}	·558	$.953\ 3659_{1671}$	7787_{24}
·509	$.961\ 1865_{1525}$	6636_{23}	·559	$.953\ 1988_{1673}$	7811_{24}
0·510	$0.961\ 0340_{1527}$	$0.000\ 6659_{24}$	**0·560**	$0.953\ 0315_{1676}$	$0.000\ 7835_{24}$
·511	$.960\ 8813_{1531}$	6683_{23}	·561	$.952\ 8639_{1680}$	7859_{23}
·512	$.960\ 7282_{1533}$	6706_{23}	·562	$.952\ 6959_{1682}$	7882_{24}
·513	$.960\ 5749_{1537}$	6729_{23}	·563	$.952\ 5277_{1685}$	7906_{24}
·514	$.960\ 4212_{1540}$	6752_{23}	·564	$.952\ 3592_{1688}$	7930_{24}
0·515	$0.960\ 2672_{1542}$	$0.000\ 6775_{23}$	**0·565**	$0.952\ 1904_{1692}$	$0.000\ 7954_{24}$
·516	$.960\ 1130_{1545}$	6798_{23}	·566	$.952\ 0212_{1694}$	7978_{24}
·517	$.959\ 9585_{1549}$	6821_{24}	·567	$.951\ 8518_{1697}$	8002_{24}
·518	$.959\ 8036_{1551}$	6845_{23}	·568	$.951\ 6821_{1700}$	8026_{24}
·519	$.959\ 6485_{1555}$	6868_{23}	·569	$.951\ 5121_{1703}$	8050_{24}
0·520	$0.959\ 4930_{1557}$	$0.000\ 6891_{23}$	**0·570**	$0.951\ 3418_{1706}$	$0.000\ 8074_{24}$
·521	$.959\ 3373_{1560}$	6914_{24}	·571	$.951\ 1712_{1709}$	8098_{24}
·522	$.959\ 1813_{1564}$	6938_{23}	·572	$.951\ 0003_{1712}$	8122_{24}
·523	$.959\ 0249_{1566}$	6961_{23}	·573	$.950\ 8291_{1715}$	8146_{24}
·524	$.958\ 8683_{1569}$	6984_{23}	·574	$.950\ 6576_{1718}$	8170_{24}
0·525	$0.958\ 7114_{1573}$	$0.000\ 7007_{24}$	**0·575**	$0.950\ 4858_{1721}$	$0.000\ 8194_{24}$
·526	$.958\ 5541_{1575}$	7031_{23}	·576	$.950\ 3137_{1724}$	8218_{24}
·527	$.958\ 3966_{1578}$	7054_{24}	·577	$.950\ 1413_{1727}$	8243_{25}
·528	$.958\ 2388_{1581}$	7078_{23}	·578	$.949\ 9686_{1729}$	8267_{24}
·529	$.958\ 0807_{1584}$	7101_{23}	·579	$.949\ 7957_{1733}$	8291_{24}
0·530	$0.957\ 9223_{1588}$	$0.000\ 7124_{24}$	**0·580**	$0.949\ 6224_{1736}$	$0.000\ 8315_{24}$
·531	$.957\ 7635_{1590}$	7148_{23}	·581	$.949\ 4488_{1739}$	8339_{24}
·532	$.957\ 6045_{1593}$	7171_{24}	·582	$.949\ 2749_{1741}$	8363_{24}
·533	$.957\ 4452_{1596}$	7195_{23}	·583	$.949\ 1008_{1745}$	8387_{24}
·534	$.957\ 2856_{1599}$	7218_{24}	·584	$.948\ 9263_{1748}$	8411_{25}
0·535	$0.957\ 1257_{1602}$	$0.000\ 7242_{23}$	**0·585**	$0.948\ 7515_{1750}$	$0.000\ 8436_{24}$
·536	$.956\ 9655_{1605}$	7265_{24}	·586	$.948\ 5765_{1754}$	8460_{24}
·537	$.956\ 8050_{1608}$	7289_{23}	·587	$.948\ 4011_{1756}$	8484_{24}
·538	$.956\ 6442_{1611}$	7312_{24}	·588	$.948\ 2255_{1760}$	8508_{24}
·539	$.956\ 4831_{1614}$	7336_{24}	·589	$.948\ 0495_{1762}$	8532_{24}
0·540	$0.956\ 3217_{1617}$	$0.000\ 7360_{23}$	**0·590**	$0.947\ 8733_{1766}$	$0.000\ 8556_{25}$
·541	$.956\ 1600_{1619}$	7383_{24}	·591	$.947\ 6967_{1768}$	8581_{24}
·542	$.955\ 9981_{1623}$	7407_{23}	·592	$.947\ 5199_{1772}$	8605_{24}
·543	$.955\ 8358_{1626}$	7430_{24}	·593	$.947\ 3427_{1774}$	8629_{24}
·544	$.955\ 6732_{1629}$	7454_{24}	·594	$.947\ 1653_{1777}$	$·8653_{25}$
0·545	$0.955\ 5103_{1631}$	$0.000\ 7478_{23}$	**0·595**	$0.946\ 9876_{1781}$	$0.000\ 8678_{24}$
·546	$.955\ 3472_{1635}$	7501_{24}	·596	$.946\ 8095_{1783}$	8702_{24}
·547	$.955\ 1837_{1638}$	7525_{24}	·597	$.946\ 6312_{1786}$	8726_{24}
·548	$.955\ 0199_{1641}$	7549_{24}	·598	$.946\ 4526_{1789}$	8750_{25}
·549	$.954\ 8558_{1643}$	7573_{23}	·599	$.946\ 2737_{1792}$	8775_{24}
0·550	$0.954\ 6915$	$0.000\ 7596$	**0·600**	$0.946\ 0945$	$0.000\ 8799$

TABLES FOR HYPERBOLIC MOTION.*

By Harley Wood, M.Sc.

In this article tables are given for the representation of hyperbolic Keplerian motion. They are based on the same formulæ, with the same numerical coefficients, prepared and intended for use in the same way as those in the previous article, " Tables for Nearly Parabolic Elliptic Motion " (Wood, 1951) and so only a few remarks need be added.

In order to avoid the use of imaginary arguments and give these tables a slightly different appearance from the previous ones we set $\alpha = -\varepsilon = (e-1)/(e+1)$. The arguments for the respective tables then become $\alpha^{\frac{1}{2}}\mu$, α and $\alpha^{\frac{1}{2}}\sigma$.

A was calculated from the series when $\alpha^{\frac{1}{2}}\mu \leqslant 0 \cdot 20$ and thereafter by obtaining $\sinh^{-1}\alpha^{\frac{1}{2}}\mu = \log\{\alpha^{\frac{1}{2}}\mu + (\alpha\mu^2+1)^{\frac{1}{2}}\}$ with the *Table of Natural Logarithms* of the " Federal Works Agency " (1941).

The signs of both h and K become negative for $e>1$ (ε negative) but since only their product appears in the formula they are tabulated as positive.

Using the manuscript tables to two places beyond what are recorded here the values of R for the hyperbolic case were calculated from equation (4) of the previous article, μ first having been obtained from equation (2). The intervals of α and $\alpha^{\frac{1}{2}}\sigma$ at which this was done were the same as before and the greatest value of R obtained was 8 units of the ninth decimal place. R is again negligible in seven figure work.

References.

Federal Works Agency Projects Administration, 1941. Table of Natural Logarithms, Volume III, New York.

Wood, H., 1951. This Journal, 84, 134. Also Sydney Obs. Papers No. 14.

HARLEY WOOD.

TABLE 1.

$\alpha^{\frac12}\mu$	A	I	N
0·000	1·000 0000$_{4}$	3·0000$_{0}$	1·000 0000$_{2}$
·001	0·999 9996$_{14}$	·0000$_{0}$	0·999 9998$_{8}$
·002	·999 9982$_{22}$	·0000$_{0}$	·999 9990$_{12}$
·003	·999 9960$_{32}$	·0000$_{0}$	·999 9978$_{18}$
·004	·999 9928$_{40}$	3·0000$_{1}$	·999 9960$_{22}$
0·005	0·999 9888$_{50}$	2·9999$_{0}$	0·999 9938$_{28}$
·006	·999 9838$_{58}$	·9999$_{0}$	·999 9910$_{32}$
·007	·999 9780$_{68}$	·9999$_{0}$	·999 9878$_{38}$
·008	·999 9712$_{76}$	·9999$_{1}$	·999 9840$_{42}$
·009	·999 9636$_{86}$	·9998$_{0}$	·999 9798$_{48}$
0·010	0·999 9550$_{94}$	2·9998$_{1}$	0·999 9750$_{52}$
·011	·999 9456$_{104}$	·9997$_{0}$	·999 9698$_{58}$
·012	·999 9352$_{112}$	·9997$_{1}$	·999 9640$_{62}$
·013	·999 9240$_{122}$	·9996$_{1}$	·999 9578$_{68}$
·014	·999 9118$_{130}$	·9996$_{0}$	·999 9510$_{72}$
0·015	0·999 8988$_{140}$	2·9995$_{1}$	0·999 9438$_{78}$
·016	·999 8848$_{148}$	·9994$_{1}$	·999 9360$_{82}$
·017	·999 8700$_{158}$	·9994$_{0}$	·999 9278$_{88}$
·018	·999 8542$_{166}$	·9993$_{1}$	·999 9190$_{92}$
·019	·999 8376$_{176}$	·9992$_{1}$	·999 9098$_{98}$
0·020	0·999 8200$_{184}$	2·9991$_{1}$	0·999 9000$_{102}$
·021	·999 8016$_{193}$	·9990$_{1}$	·999 8898$_{108}$
·022	·999 7823$_{203}$	·9989$_{1}$	·999 8790$_{112}$
·023	·999 7620$_{211}$	·9988$_{1}$	·999 8678$_{118}$
·024	·999 7409$_{220}$	·9987$_{1}$	·999 8560$_{122}$
0·025	0·999 7189$_{230}$	2·9986$_{1}$	0·999 8438$_{127}$
·026	·999 6959$_{238}$	·9985$_{1}$	·999 8311$_{133}$
·027	·999 6721$_{247}$	·9984$_{2}$	·999 8178$_{137}$
·028	·999 6474$_{257}$	·9982$_{1}$	·999 8041$_{143}$
·029	·999 6217$_{265}$	·9981$_{1}$	·999 7898$_{147}$
0·030	0·999 5952$_{274}$	2·9980$_{2}$	0·999 7751$_{152}$
·031	·999 5678$_{283}$	·9978$_{1}$	·999 7599$_{158}$
·032	·999 5395$_{292}$	·9977$_{1}$	·999 7441$_{162}$
·033	·999 5103$_{301}$	·9976$_{2}$	·999 7279$_{167}$
·034	·999 4802$_{310}$	·9974$_{2}$	·999 7112$_{173}$
0·035	0·999 4492$_{320}$	2·9972$_{1}$	0·999 6939$_{177}$
·036	·999 4172$_{327}$	·9971$_{2}$	·999 6762$_{182}$
·037	·999 3845$_{337}$	·9969$_{1}$	·999 6580$_{187}$
·038	·999 3508$_{346}$	·9968$_{2}$	·999 6393$_{193}$
·039	·999 3162$_{355}$	·9966$_{2}$	·999 6200$_{197}$
0·040	0·999 2807$_{364}$	2·9964$_{2}$	0·999 6003$_{202}$
·041	·999 2443$_{373}$	·9962$_{2}$	·999 5801$_{207}$
·042	·999 2070$_{381}$	·9960$_{2}$	·999 5594$_{212}$
·043	·999 1689$_{391}$	·9958$_{1}$	·999 5382$_{217}$
·044	·999 1298$_{400}$	·9957$_{2}$	·999 5165$_{222}$
0·045	0·999 0898$_{408}$	2·9955$_{3}$	0·999 4943$_{227}$
·046	·999 0490$_{417}$	·9952$_{3}$	·999 4716$_{232}$
·047	·999 0073$_{427}$	·9950$_{2}$	·999 4484$_{237}$
·048	·998 9646$_{435}$	·9948$_{2}$	·999 4247$_{242}$
·049	·998 9211$_{444}$	·9946$_{2}$	·999 4005$_{247}$
0·050	0·998 8767	2·9944	0·999 3758

$\alpha^{\frac12}\mu$	A 0·	I 2·	N 0·
0·050	9988 767$_{453}$	9944$_{2}$	9993 758$_{252}$
·051	9988 314$_{462}$	9942$_{2}$	9993 506$_{257}$
·052	9987 852$_{471}$	9939$_{2}$	9993 249$_{262}$
·053	9987 381$_{480}$	9937$_{2}$	9992 987$_{266}$
·054	9986 901$_{489}$	9935$_{3}$	9992 721$_{272}$
0·055	9986 412$_{498}$	9932$_{2}$	9992 449$_{277}$
·056	9985 914$_{506}$	9930$_{2}$	9992 172$_{281}$
·057	9985 408$_{516}$	9927$_{3}$	9991 891$_{287}$
·058	9984 892$_{524}$	9925$_{2}$	9991 604$_{291}$
·059	9984 368$_{533}$	9922$_{3}$	9991 313$_{297}$
0·060	9983 835$_{543}$	9919$_{2}$	9991 016$_{301}$
·061	9983 292$_{551}$	9917$_{3}$	9990 715$_{307}$
·062	9982 741$_{559}$	9914$_{3}$	9990 408$_{311}$
·063	9982 182$_{569}$	9911$_{3}$	9990 097$_{316}$
·064	9981 613$_{578}$	9908$_{3}$	9989 781$_{321}$
0·065	9981 035$_{586}$	9905$_{3}$	9989 460$_{326}$
·066	9980 449$_{596}$	9902$_{3}$	9989 134$_{331}$
·067	9979 853$_{604}$	9899$_{3}$	9988 803$_{336}$
·068	9979 249$_{613}$	9896$_{3}$	9988 467$_{341}$
·069	9978 636$_{622}$	9893$_{3}$	9988 126$_{346}$
0·070	9978 014$_{631}$	9890$_{3}$	9987 780$_{351}$
·071	9977 383$_{639}$	9887$_{3}$	9987 429$_{356}$
·072	9976 744$_{649}$	9884$_{3}$	9987 073$_{360}$
·073	9976 095$_{657}$	9881$_{3}$	9986 713$_{366}$
·074	9975 438$_{666}$	9877$_{3}$	9986 347$_{370}$
0·075	9974 772$_{675}$	9874$_{3}$	9985 977$_{375}$
·076	9974 097$_{684}$	9871$_{3}$	9985 602$_{381}$
·077	9973 413$_{692}$	9867$_{4}$	9985 221$_{385}$
·078	9972 721$_{702}$	9864$_{3}$	9984 836$_{390}$
·079	9972 019$_{710}$	9860$_{3}$	9984 446$_{395}$
0·080	9971 309$_{719}$	9857$_{4}$	9984 051$_{400}$
·081	9970 590$_{727}$	9853$_{4}$	9983 651$_{405}$
·082	9969 863$_{737}$	9850$_{3}$	9983 246$_{409}$
·083	9969 126$_{745}$	9846$_{4}$	9982 837$_{415}$
·084	9968 381$_{754}$	9842$_{4}$	9982 422$_{420}$
0·085	9967 627$_{763}$	9838$_{3}$	9982 002$_{424}$
·086	9966 864$_{772}$	9835$_{3}$	9981 578$_{429}$
·087	9966 092$_{780}$	9831$_{4}$	9981 149$_{434}$
·088	9965 312$_{789}$	9827$_{4}$	9980 715$_{439}$
·089	9964 523$_{798}$	9823$_{4}$	9980 276$_{444}$
0·090	9963 725$_{807}$	9819$_{4}$	9979 832$_{449}$
·091	9962 918$_{815}$	9815$_{4}$	9979 383$_{454}$
·092	9962 103$_{824}$	9811$_{4}$	9978 929$_{459}$
·093	9961 279$_{833}$	9807$_{4}$	9978 470$_{463}$
·094	9960 446$_{842}$	9803$_{5}$	9978 007$_{468}$
0·095	9959 604$_{850}$	9798$_{4}$	9977 539$_{473}$
·096	9958 754$_{859}$	9794$_{4}$	9977 066$_{478}$
·097	9957 895$_{868}$	9790$_{4}$	9976 588$_{483}$
·098	9957 027$_{876}$	9786$_{5}$	9976 105$_{488}$
·099	9956 151$_{885}$	9781$_{4}$	9975 617$_{493}$
0·100	9955 266	9777	9975 124

TABLE 1.

$\alpha^i\mu$	A	I	N	$\alpha^i\mu$	A	I	N
	0·	2·	0·		0·	2·	0·
0·100	$9955\ 266$	9777_5	$9975\ 124$	0·150	$9900\ 086$	9503_6	$9944\ 374$
·101	$9954\ 372_{894}$	9772_5	$9974\ 627^{497}$	·151	$9898\ 767_{1319}$	9497_6	$9943\ 638^{736}$
·102	$9953\ 470_{902}$	9768_4	$9974\ 124^{503}$	·152	$9897\ 440_{1327}$	9490_7	$9942\ 898^{740}$
·103	$9952\ 559_{911}$	9763_5	$9973\ 617^{507}$	·153	$9896\ 104_{1336}$	9483_7	$9942\ 153^{745}$
·104	$9951\ 639_{920}$	9759_4	$9973\ 105^{512}$	·154	$9894\ 761_{1343}$	9477_6	$9941\ 403^{750}$
0·105	$9950\ 711_{928}$	9754_4	$9972\ 588^{517}$	0·155	$9893\ 409_{1352}$	9470_7	$9940\ 648^{755}$
·106	$9949\ 774_{937}$	9750_4	$9972\ 067^{521}$	·156	$9892\ 049_{1360}$	9463_7	$9939\ 889^{759}$
·107	$9948\ 828_{946}$	9745_5	$9971\ 540^{527}$	·157	$9890\ 680_{1369}$	9457_6	$9939\ 125^{764}$
·108	$9947\ 874_{954}$	9740_5	$9971\ 009^{531}$	·158	$9889\ 303_{1377}$	9450_7	$9938\ 357^{768}$
·109	$9946\ 911_{963}$	9735_5	$9970\ 473^{536}$	·159	$9887\ 919_{1384}$	9443_7	$9937\ 584^{773}$
0·110	$9945\ 939_{972}$	9730_5	$9969\ 932^{541}$	0·160	$9886\ 525_{1394}$	9436_7	$9936\ 806^{778}$
·111	$9944\ 959_{980}$	9726_4	$9969\ 386^{546}$	·161	$9885\ 124_{1401}$	9429_7	$9936\ 024^{782}$
·112	$9943\ 970_{989}$	9721_5	$9968\ 835^{551}$	·162	$9883\ 715_{1409}$	9422_7	$9935\ 237^{787}$
·113	$9942\ 972_{998}$	9716_5	$9968\ 280^{555}$	·163	$9882\ 297_{1418}$	9415_7	$9934\ 446^{791}$
·114	$9941\ 966_{1006}$	9711_5	$9967\ 719^{561}$	·164	$9880\ 871_{1426}$	9408_7	$9933\ 649^{797}$
0·115	$9940\ 952_{1014}$	9706_5	$9967\ 154^{565}$	0·165	$9879\ 437_{1434}$	9401_7	$9932\ 849^{800}$
·116	$9939\ 929_{1023}$	9701_5	$9966\ 584^{570}$	·166	$9877\ 995_{1442}$	9394_7	$9932\ 043^{806}$
·117	$9938\ 897_{1032}$	9695_6	$9966\ 010^{574}$	·167	$9876\ 544_{1451}$	9387_7	$9931\ 233^{810}$
·118	$9937\ 856_{1041}$	9690_5	$9965\ 430^{580}$	·168	$9875\ 086_{1458}$	9380_7	$9930\ 419^{814}$
·119	$9936\ 808_{1048}$	9685_5	$9964\ 846^{584}$	·169	$9873\ 619_{1467}$	9372_7	$9929\ 599^{820}$
0·120	$9935\ 750_{1058}$	9680_5	$9964\ 257^{589}$	0·170	$9872\ 144_{1475}$	9365_7	$9928\ 776^{823}$
·121	$9934\ 684_{1066}$	9675_5	$9963\ 663^{594}$	·171	$9870\ 661_{1483}$	9358_7	$9927\ 947^{829}$
·122	$9933\ 609_{1075}$	9669_6	$9963\ 064^{599}$	·172	$9869\ 170_{1491}$	9350_8	$9927\ 114^{833}$
·123	$9932\ 526_{1083}$	9664_6	$9962\ 461^{603}$	·173	$9867\ 671_{1499}$	9343_7	$9926\ 277^{837}$
·124	$9931\ 435_{1091}$	9658_6	$9961\ 853^{608}$	·174	$9866\ 164_{1507}$	9336_8	$9925\ 435^{842}$
0·125	$9930\ 335_{1100}$	9653_6	$9961\ 240^{613}$	0·175	$9864\ 648_{1516}$	9328_7	$9924\ 588^{847}$
·126	$9929\ 226_{1109}$	9647_5	$9960\ 622^{618}$	·176	$9863\ 125_{1523}$	9321_8	$9923\ 737^{851}$
·127	$9928\ 109_{1117}$	9642_5	$9959\ 999^{623}$	·177	$9861\ 594_{1531}$	9313_8	$9922\ 881^{856}$
·128	$9926\ 983_{1126}$	9636_6	$9959\ 372^{627}$	·178	$9860\ 054_{1540}$	9305_8	$9922\ 021^{860}$
·129	$9925\ 849_{1134}$	9631_5	$9958\ 740^{632}$	·179	$9858\ 507_{1547}$	9298_7	$9921\ 156^{865}$
0·130	$9924\ 706_{1143}$	9625_6	$9958\ 103^{637}$	0·180	$9856\ 951_{1556}$	9290_8	$9920\ 286^{870}$
·131	$9923\ 555_{1151}$	9619_6	$9957\ 462^{641}$	·181	$9855\ 388_{1563}$	9282_7	$9919\ 412^{874}$
·132	$9922\ 396_{1159}$	9614_5	$9956\ 815^{647}$	·182	$9853\ 816_{1572}$	9275_7	$9918\ 534^{878}$
·133	$9921\ 228_{1168}$	9608_6	$9956\ 164^{651}$	·183	$9852\ 237_{1579}$	9267_8	$9917\ 651^{883}$
·134	$9920\ 051_{1177}$	9602_6	$9955\ 509^{655}$	·184	$9850\ 649_{1588}$	9259_8	$9916\ 763^{888}$
0·135	$9918\ 866_{1185}$	9596_6	$9954\ 848^{661}$	0·185	$9849\ 054_{1595}$	9251_8	$9915\ 871^{892}$
·136	$9917\ 673_{1193}$	9590_6	$9954\ 183^{665}$	·186	$9847\ 450_{1604}$	9243_8	$9914\ 975^{896}$
·137	$9916\ 471_{1202}$	9584_6	$9953\ 513^{670}$	·187	$9845\ 839_{1611}$	9235_8	$9914\ 073^{902}$
·138	$9915\ 261_{1210}$	9578_6	$9952\ 838^{675}$	·188	$9844\ 220_{1619}$	9227_8	$9913\ 168^{905}$
·139	$9914\ 042_{1219}$	9572_6	$9952\ 159^{679}$	·189	$9842\ 592_{1628}$	9219_8	$9912\ 258^{910}$
0·140	$9912\ 815_{1227}$	9566_6	$9951\ 474^{685}$	0·190	$9840\ 957_{1635}$	9211_8	$9911\ 343^{915}$
·141	$9911\ 580_{1235}$	9560_6	$9950\ 786^{688}$	·191	$9839\ 314_{1643}$	9203_8	$9910\ 424^{919}$
·142	$9910\ 336_{1244}$	9554_6	$9950\ 092^{694}$	·192	$9837\ 663_{1651}$	9195_8	$9909\ 501^{923}$
·143	$9909\ 084_{1252}$	9548_7	$9949\ 394^{698}$	·193	$9836\ 004_{1659}$	9187_8	$9908\ 572^{929}$
·144	$9907\ 824_{1260}$	9541_6	$9948\ 691^{703}$	·194	$9834\ 338_{1666}$	9179_8	$9907\ 640^{932}$
0·145	$9906\ 555_{1269}$	9535_6	$9947\ 983^{708}$	0·195	$9832\ 663_{1675}$	9171_9	$9906\ 703^{937}$
·146	$9905\ 278_{1277}$	9529_7	$9947\ 271^{712}$	·196	$9830\ 980_{1683}$	9162_8	$9905\ 762^{941}$
·147	$9903\ 992_{1286}$	9522_6	$9946\ 553^{718}$	·197	$9829\ 290_{1690}$	9154_8	$9904\ 816^{946}$
·148	$9902\ 698_{1294}$	9516_6	$9945\ 832^{721}$	·198	$9827\ 592_{1698}$	9146_8	$9903\ 865^{951}$
·149	$9901\ 396_{1302}$	9510_7	$9945\ 105^{727}$	·199	$9825\ 886_{1706}$	9137_9	$9902\ 911^{954}$
0·150	$9900\ 086_{1310}$	9503	$9944\ 374^{731}$	0·200	$9824\ 172_{1714}$	9129	$9901\ 951^{960}$

TABLE 1.

$\alpha^{\frac{1}{2}}\mu$	A	I	N	$\alpha^{\frac{1}{2}}\mu$	A	I	N
	0·	2·	0·		0·	2·	0·
0·200	$9824\ 172_{1721}$	$9129_{\,8}$	$9901\ 951_{963}$	0·250	$9728\ 788_{2097}$	$8663_{\,10}$	$9848\ 450_{1178}$
·201	$9822\ 451_{1729}$	$9121_{\,8}$	$9900\ 988_{968}$	·251	$9726\ 691_{2103}$	$8653_{\,10}$	$9847\ 272_{1183}$
·202	$9820\ 722_{1738}$	$9112_{\,9}$	$9900\ 020_{973}$	·252	$9724\ 588_{2111}$	$8643_{\,10}$	$9846\ 089_{1186}$
·203	$9818\ 984_{1744}$	$9104_{\,8}$	$9899\ 047_{977}$	·253	$9722\ 477_{2117}$	$8633_{\,11}$	$9844\ 903_{1191}$
·204	$9817\ 240_{1753}$	$9095_{\,9}$	$9898\ 070_{981}$	·254	$9720\ 360_{2125}$	$8622_{\,10}$	$9843\ 712_{1195}$
0·205	$9815\ 487_{1760}$	$9086_{\,8}$	$9897\ 089_{986}$	0·255	$9718\ 235_{2132}$	$8612_{\,10}$	$9842\ 517_{1199}$
·206	$9813\ 727_{1769}$	$9078_{\,9}$	$9896\ 103_{990}$	·256	$9716\ 103_{2139}$	$8602_{\,10}$	$9841\ 318_{1203}$
·207	$9811\ 958_{1775}$	$9069_{\,9}$	$9895\ 113_{995}$	·257	$9713\ 964_{2146}$	$8591_{\,10}$	$9840\ 115_{1207}$
·208	$9810\ 183_{1784}$	$9060_{\,8}$	$9894\ 118_{999}$	·258	$9711\ 818_{2154}$	$8581_{\,11}$	$9838\ 908_{1211}$
·209	$9808\ 399_{1791}$	$9052_{\,9}$	$9893\ 119_{1003}$	·259	$9709\ 664_{2160}$	$8570_{\,10}$	$9837\ 697_{1215}$
0·210	$9806\ 608_{1799}$	$9043_{\,9}$	$9892\ 116_{1008}$	0·260	$9707\ 504_{2167}$	$8560_{\,11}$	$9836\ 482_{1220}$
·211	$9804\ 809_{1807}$	$9034_{\,9}$	$9891\ 108_{1012}$	·261	$9705\ 337_{2175}$	$8549_{\,10}$	$9835\ 262_{1223}$
·212	$9803\ 002_{1814}$	$9025_{\,9}$	$9890\ 096_{1016}$	·262	$9703\ 162_{2181}$	$8539_{\,11}$	$9834\ 039_{1228}$
·213	$9801\ 188_{1822}$	$9016_{\,9}$	$9889\ 080_{1021}$	·263	$9700\ 981_{2189}$	$8528_{\,10}$	$9832\ 811_{1231}$
·214	$9799\ 366_{1829}$	$9007_{\,9}$	$9888\ 059_{1025}$	·264	$9698\ 792_{2195}$	$8518_{\,11}$	$9831\ 580_{1236}$
0·215	$9797\ 537_{1837}$	$8998_{\,9}$	$9887\ 034_{1030}$	0·265	$9696\ 597_{2203}$	$8507_{\,11}$	$9830\ 344_{1240}$
·216	$9795\ 700_{1845}$	$8989_{\,9}$	$9886\ 004_{1034}$	·266	$9694\ 394_{2209}$	$8496_{\,10}$	$9829\ 104_{1243}$
·217	$9793\ 855_{1852}$	$8980_{\,9}$	$9884\ 970_{1038}$	·267	$9692\ 185_{2217}$	$8486_{\,11}$	$9827\ 861_{1248}$
·218	$9792\ 003_{1860}$	$8971_{\,9}$	$9883\ 932_{1043}$	·268	$9689\ 968_{2223}$	$8475_{\,11}$	$9826\ 613_{1252}$
·219	$9790\ 143_{1868}$	$8962_{\,9}$	$9882\ 889_{1046}$	·269	$9687\ 745_{2230}$	$8464_{\,11}$	$9825\ 361_{1256}$
0·220	$9788\ 275_{1875}$	$8953_{\,9}$	$9881\ 843_{1052}$	0·270	$9685\ 515_{2238}$	$8453_{\,10}$	$9824\ 105_{1260}$
·221	$9786\ 400_{1883}$	$8944_{\,9}$	$9880\ 791_{1055}$	·271	$9683\ 277_{2244}$	$8443_{\,11}$	$9822\ 845_{1264}$
·222	$9784\ 517_{1890}$	$8935_{\,9}$	$9879\ 736_{1060}$	·272	$9681\ 033_{2251}$	$8432_{\,11}$	$9821\ 581_{1268}$
·223	$9782\ 627_{1897}$	$8926_{\,9}$	$9878\ 676_{1064}$	·273	$9678\ 782_{2258}$	$8421_{\,11}$	$9820\ 313_{1272}$
·224	$9780\ 730_{1906}$	$8916_{\,9}$	$9877\ 612_{1069}$	·274	$9676\ 524_{2264}$	$8410_{\,11}$	$9819\ 041_{1276}$
0·225	$9778\ 824_{1912}$	$8907_{\,9}$	$9876\ 543_{1073}$	0·275	$9674\ 260_{2272}$	$8399_{\,11}$	$9817\ 765_{1279}$
·226	$9776\ 912_{1921}$	$8898_{\,10}$	$9875\ 470_{1077}$	·276	$9671\ 988_{2278}$	$8388_{\,11}$	$9816\ 486_{1284}$
·227	$9774\ 991_{1927}$	$8888_{\,9}$	$9874\ 393_{1081}$	·277	$9669\ 710_{2286}$	$8377_{\,11}$	$9815\ 202_{1288}$
·228	$9773\ 064_{1935}$	$8879_{\,10}$	$9873\ 312_{1086}$	·278	$9667\ 424_{2292}$	$8366_{\,11}$	$9813\ 914_{1292}$
·229	$9771\ 129_{1943}$	$8869_{\,9}$	$9872\ 226_{1090}$	·279	$9665\ 132_{2299}$	$8355_{\,11}$	$9812\ 622_{1296}$
0·230	$9769\ 186_{1950}$	$8860_{\,10}$	$9871\ 136_{1094}$	0·280	$9662\ 833_{2305}$	$8344_{\,11}$	$9811\ 326_{1299}$
·231	$9767\ 236_{1958}$	$8850_{\,9}$	$9870\ 042_{1098}$	·281	$9660\ 528_{2313}$	$8333_{\,11}$	$9810\ 027_{1304}$
·232	$9765\ 278_{1964}$	$8841_{\,10}$	$9868\ 944_{1103}$	·282	$9658\ 215_{2319}$	$8322_{\,12}$	$9808\ 723_{1308}$
·233	$9763\ 314_{1973}$	$8831_{\,9}$	$9867\ 841_{1107}$	·283	$9655\ 896_{2326}$	$8310_{\,11}$	$9807\ 415_{1311}$
·234	$9761\ 341_{1979}$	$8822_{\,10}$	$9866\ 734_{1111}$	·284	$9653\ 570_{2333}$	$8299_{\,11}$	$9806\ 104_{1316}$
0·235	$9759\ 362_{1988}$	$8812_{\,10}$	$9865\ 623_{1115}$	0·285	$9651\ 237_{2339}$	$8288_{\,11}$	$9804\ 788_{1319}$
·236	$9757\ 374_{1994}$	$8802_{\,9}$	$9864\ 508_{1120}$	·286	$9648\ 898_{2346}$	$8277_{\,12}$	$9803\ 469_{1324}$
·237	$9755\ 380_{2002}$	$8793_{\,10}$	$9863\ 388_{1124}$	·287	$9646\ 552_{2353}$	$8265_{\,11}$	$9802\ 145_{1327}$
·238	$9753\ 378_{2009}$	$8783_{\,10}$	$9862\ 264_{1128}$	·288	$9644\ 199_{2359}$	$8254_{\,11}$	$9800\ 818_{1331}$
·239	$9751\ 369_{2016}$	$8773_{\,10}$	$9861\ 136_{1132}$	·289	$9641\ 840_{2366}$	$8243_{\,12}$	$9799\ 487_{1335}$
0·240	$9749\ 353_{2024}$	$8763_{\,10}$	$9860\ 004_{1137}$	0·290	$9639\ 474_{2373}$	$8231_{\,11}$	$9798\ 152_{1339}$
·241	$9747\ 329_{2031}$	$8753_{\,10}$	$9858\ 867_{1141}$	·291	$9637\ 101_{2379}$	$8220_{\,12}$	$9796\ 813_{1343}$
·242	$9745\ 298_{2039}$	$8743_{\,9}$	$9857\ 726_{1145}$	·292	$9634\ 722_{2386}$	$8208_{\,11}$	$9795\ 470_{1346}$
·243	$9743\ 259_{2045}$	$8734_{\,10}$	$9856\ 581_{1149}$	·293	$9632\ 336_{2393}$	$8197_{\,12}$	$9794\ 124_{1351}$
·244	$9741\ 214_{2053}$	$8724_{\,10}$	$9855\ 432_{1153}$	·294	$9629\ 943_{2399}$	$8185_{\,11}$	$9792\ 773_{1354}$
0·245	$9739\ 161_{2060}$	$8714_{\,10}$	$9854\ 279_{1157}$	0·295	$9627\ 544_{2406}$	$8174_{\,12}$	$9791\ 419_{1359}$
·246	$9737\ 101_{2068}$	$8704_{\,10}$	$9853\ 122_{1162}$	·296	$9625\ 138_{2412}$	$8162_{\,11}$	$9790\ 060_{1362}$
·247	$9735\ 033_{2074}$	$8694_{\,11}$	$9851\ 960_{1166}$	·297	$9622\ 726_{2419}$	$8151_{\,12}$	$9788\ 698_{1366}$
·248	$9732\ 959_{2082}$	$8683_{\,10}$	$9850\ 794_{1170}$	·298	$9620\ 307_{2425}$	$8139_{\,12}$	$9787\ 332_{1369}$
·249	$9730\ 877_{2089}$	$8673_{\,10}$	$9849\ 624_{1174}$	·299	$9617\ 882_{2432}$	$8127_{\,11}$	$9785\ 963_{1374}$
0·250	9728 788	8663	9848 450	0·300	9615 450	8116	9784 589

TABLE 1.

$\alpha^{l}\mu$	A	I	N	$\alpha^{l}\mu$	A	I	N
	0·	2·	0·		0·	2·	0·
0·300	$9615\ 450_{2439}$	8116_{12}	$9784\ 589_{1377}$	**0·350**	$9485\ 870_{2744}$	7498_{13}	$9711\ 184_{1559}$
·301	$9613\ 011_{2444}$	8104_{12}	$9783\ 212_{1382}$	·351	$9483\ 126_{2751}$	7485_{13}	$9709\ 625_{1563}$
·302	$9610\ 567_{2452}$	8092_{11}	$9781\ 830_{1385}$	·352	$9480\ 375_{2756}$	7472_{13}	$9708\ 062_{1566}$
·303	$9608\ 115_{2458}$	8081_{12}	$9780\ 445_{1388}$	·353	$9477\ 619_{2762}$	7459_{13}	$9706\ 496_{1570}$
·304	$9605\ 657_{2464}$	8069_{12}	$9779\ 057_{1393}$	·354	$9474\ 857_{2768}$	7446_{13}	$9704\ 926_{1573}$
0·305	$9603\ 193_{2470}$	8057_{12}	$9777\ 664_{1396}$	**0·355**	$9472\ 089_{2773}$	7433_{13}	$9703\ 353_{1577}$
·306	$9600\ 723_{2478}$	8045_{12}	$9776\ 268_{1401}$	·356	$9469\ 316_{2779}$	7420_{14}	$9701\ 776_{1580}$
·307	$9598\ 245_{2483}$	8033_{12}	$9774\ 867_{1404}$	·357	$9466\ 537_{2785}$	7406_{14}	$9700\ 196_{1584}$
·308	$9595\ 762_{2490}$	8021_{12}	$9773\ 463_{1407}$	·358	$9463\ 752_{2790}$	7393_{13}	$9698\ 612_{1586}$
·309	$9593\ 272_{2496}$	8009_{11}	$9772\ 056_{1412}$	·359	$9460\ 962_{2796}$	7380_{13}	$9697\ 026_{1591}$
0·310	$9590\ 776_{2503}$	7998_{12}	$9770\ 644_{1415}$	**0·360**	$9458\ 166_{2802}$	7367_{13}	$9695\ 435_{1593}$
·311	$9588\ 273_{2509}$	7986_{12}	$9769\ 229_{1419}$	·361	$9455\ 364_{2807}$	7354_{14}	$9693\ 842_{1598}$
·312	$9585\ 764_{2515}$	7974_{13}	$9767\ 810_{1423}$	·362	$9452\ 557_{2813}$	7340_{13}	$9692\ 244_{1600}$
·313	$9583\ 249_{2521}$	7961_{12}	$9766\ 387_{1426}$	·363	$9449\ 744_{2818}$	7327_{13}	$9690\ 644_{1604}$
·314	$9580\ 728_{2528}$	7949_{12}	$9764\ 961_{1430}$	·364	$9446\ 926_{2824}$	7314_{13}	$9689\ 040_{1607}$
0·315	$9578\ 200_{2535}$	7937_{12}	$9763\ 531_{1434}$	**0·365**	$9444\ 102_{2829}$	7301_{14}	$9687\ 433_{1611}$
·316	$9575\ 665_{2540}$	7925_{12}	$9762\ 097_{1438}$	·366	$9441\ 273_{2835}$	7287_{13}	$9685\ 822_{1613}$
·317	$9573\ 125_{2547}$	7913_{12}	$9760\ 659_{1441}$	·367	$9438\ 438_{2841}$	7274_{14}	$9684\ 209_{1618}$
·318	$9570\ 578_{2553}$	7901_{12}	$9759\ 218_{1445}$	·368	$9435\ 597_{2846}$	7260_{13}	$9682\ 591_{1620}$
·319	$9568\ 025_{2559}$	7889_{13}	$9757\ 773_{1449}$	·369	$9432\ 751_{2851}$	7247_{13}	$9680\ 971_{1624}$
0·320	$9565\ 466_{2565}$	7876_{12}	$9756\ 324_{1452}$	**0·370**	$9429\ 900_{2857}$	7234_{14}	$9679\ 347_{1627}$
·321	$9562\ 901_{2572}$	7864_{12}	$9754\ 872_{1456}$	·371	$9427\ 043_{2862}$	7220_{13}	$9677\ 720_{1631}$
·322	$9560\ 329_{2577}$	7852_{12}	$9753\ 416_{1460}$	·372	$9424\ 181_{2868}$	7207_{14}	$9676\ 089_{1634}$
·323	$9557\ 752_{2584}$	7840_{12}	$9751\ 956_{1463}$	·373	$9421\ 313_{2873}$	7193_{13}	$9674\ 455_{1637}$
·324	$9555\ 168_{2590}$	7827_{12}	$9750\ 493_{1467}$	·374	$9418\ 440_{2879}$	7180_{14}	$9672\ 818_{1640}$
0·325	$9552\ 578_{2597}$	7815_{12}	$9749\ 026_{1471}$	**0·375**	$9415\ 561_{2884}$	7166_{13}	$9671\ 178_{1644}$
·326	$9549\ 981_{2602}$	7803_{12}	$9747\ 555_{1474}$	·376	$9412\ 677_{2889}$	7153_{13}	$9669\ 534_{1647}$
·327	$9547\ 379_{2608}$	7790_{13}	$9746\ 081_{1478}$	·377	$9409\ 788_{2894}$	7139_{13}	$9667\ 887_{1650}$
·328	$9544\ 771_{2615}$	7778_{13}	$9744\ 603_{1482}$	·378	$9406\ 894_{2900}$	7126_{14}	$9666\ 237_{1654}$
·329	$9542\ 156_{2620}$	7765_{12}	$9743\ 121_{1485}$	·379	$9403\ 994_{2906}$	7112_{14}	$9664\ 583_{1656}$
0·330	$9539\ 536_{2627}$	7753_{13}	$9741\ 636_{1489}$	**0·380**	$9401\ 088_{2910}$	7098_{13}	$9662\ 927_{1660}$
·331	$9536\ 909_{2633}$	7740_{12}	$9740\ 147_{1492}$	·381	$9398\ 178_{2916}$	7085_{14}	$9661\ 267_{1664}$
·332	$9534\ 276_{2638}$	7728_{13}	$9738\ 655_{1496}$	·382	$9395\ 262_{2922}$	7071_{14}	$9659\ 603_{1666}$
·333	$9531\ 638_{2645}$	7715_{12}	$9737\ 159_{1499}$	·383	$9392\ 340_{2926}$	7057_{14}	$9657\ 937_{1670}$
·334	$9528\ 993_{2651}$	7703_{13}	$9735\ 660_{1504}$	·384	$9389\ 414_{2932}$	7043_{13}	$9656\ 267_{1673}$
0·335	$9526\ 342_{2657}$	7690_{13}	$9734\ 156_{1506}$	**0·385**	$9386\ 482_{2937}$	7030_{14}	$9654\ 594_{1676}$
·336	$9523\ 685_{2662}$	7677_{12}	$9732\ 650_{1511}$	·386	$9383\ 545_{2942}$	7016_{14}	$9652\ 918_{1679}$
·337	$9521\ 023_{2669}$	7665_{13}	$9731\ 139_{1513}$	·387	$9380\ 603_{2947}$	7002_{14}	$9651\ 239_{1683}$
·338	$9518\ 354_{2675}$	7652_{13}	$9729\ 626_{1518}$	·388	$9377\ 656_{2953}$	6988_{14}	$9649\ 556_{1685}$
·339	$9515\ 679_{2680}$	7639_{12}	$9728\ 108_{1521}$	·389	$9374\ 703_{2957}$	6975_{14}	$9647\ 871_{1689}$
0·340	$9512\ 999_{2687}$	7627_{13}	$9726\ 587_{1524}$	**0·390**	$9371\ 746_{2963}$	6961_{14}	$9646\ 182_{1692}$
·341	$9510\ 312_{2692}$	7614_{13}	$9725\ 063_{1528}$	·391	$9368\ 783_{2968}$	6947_{14}	$9644\ 490_{1695}$
·342	$9507\ 620_{2698}$	7601_{13}	$9723\ 535_{1532}$	·392	$9365\ 815_{2973}$	6933_{14}	$9642\ 795_{1699}$
·343	$9504\ 922_{2704}$	7588_{13}	$9722\ 003_{1535}$	·393	$9362\ 842_{2979}$	6919_{14}	$9641\ 096_{1701}$
·344	$9502\ 218_{2710}$	7575_{12}	$9720\ 468_{1538}$	·394	$9359\ 863_{2983}$	6905_{14}	$9639\ 395_{1705}$
0·345	$9499\ 508_{2716}$	7563_{13}	$9718\ 930_{1542}$	**0·395**	$9356\ 880_{2988}$	6891_{14}	$9637\ 690_{1708}$
·346	$9496\ 792_{2722}$	7550_{13}	$9717\ 388_{1546}$	·396	$9353\ 892_{2994}$	6877_{14}	$9635\ 982_{1710}$
·347	$9494\ 070_{2727}$	7537_{13}	$9715\ 842_{1549}$	·397	$9350\ 898_{2998}$	6863_{14}	$9634\ 272_{1714}$
·348	$9491\ 343_{2734}$	7524_{13}	$9714\ 293_{1553}$	·398	$9347\ 900_{3004}$	6849_{14}	$9632\ 558_{1718}$
·349	$9488\ 609_{2739}$	7511_{13}	$9712\ 740_{1556}$	·399	$9344\ 896_{3008}$	6835_{14}	$9630\ 840_{1720}$
0·350	$9485\ 870$	7498	$9711\ 184$	**0·400**	$9341\ 888$	6821	$9629\ 120$

HARLEY WOOD.

TABLE 1.

$\alpha^{\frac12}\mu$	A 0·	I 2·	N 0·	$\alpha^{\frac12}\mu$	A 0·	I 2·	N 0·
0·400	$9341\ 888_{3014}$	6821_{14}	$9629\ 120_{1723}$	**0·450**	$9185\ 403_{3244}$	6097_{15}	$9539\ 320_{1869}$
·401	$9338\ 874_{3018}$	6807_{14}	$9627\ 397_{1727}$	·451	$9182\ 159_{3248}$	6082_{14}	$9537\ 451_{1871}$
·402	$9335\ 856_{3024}$	6793_{14}	$9625\ 670_{1729}$	·452	$9178\ 911_{3253}$	6068_{14}	$9535\ 580_{1874}$
·403	$9332\ 832_{3028}$	6779_{14}	$9623\ 941_{1733}$	·453	$9175\ 658_{3256}$	6053_{15}	$9533\ 706_{1877}$
·404	$9329\ 804_{3034}$	6765_{14}	$9622\ 208_{1735}$	·454	$9172\ 402_{3261}$	6038_{15}	$9531\ 829_{1879}$
0·405	$9326\ 770_{3038}$	6751_{14}	$9620\ 473_{1739}$	**0·455**	$9169\ 141_{3265}$	6023_{15}	$9529\ 950_{1882}$
·406	$9323\ 732_{3043}$	6737_{14}	$9618\ 734_{1742}$	·456	$9165\ 876_{3269}$	6008_{15}	$9528\ 068_{1885}$
·407	$9320\ 689_{3048}$	6722_{15}	$9616\ 992_{1744}$	·457	$9162\ 607_{3274}$	5993_{15}	$9526\ 183_{1887}$
·408	$9317\ 641_{3053}$	6708_{14}	$9615\ 248_{1748}$	·458	$9159\ 333_{3277}$	5978_{15}	$9524\ 296_{1890}$
·409	$9314\ 588_{3058}$	6694_{14}	$9613\ 500_{1751}$	·459	$9156\ 056_{3282}$	5963_{15}	$9522\ 406_{1893}$
0·410	$9311\ 530_{3063}$	6680_{14}	$9611\ 749_{1754}$	**0·460**	$9152\ 774_{3285}$	5948_{15}	$9520\ 513_{1895}$
·411	$9308\ 467_{3068}$	6666_{15}	$9609\ 995_{1757}$	·461	$9149\ 489_{3290}$	5933_{15}	$9518\ 618_{1898}$
·412	$9305\ 399_{3072}$	6651_{14}	$9608\ 238_{1760}$	·462	$9146\ 199_{3294}$	5918_{15}	$9516\ 720_{1900}$
·413	$9302\ 327_{3077}$	6637_{14}	$9606\ 478_{1762}$	·463	$9142\ 905_{3297}$	5903_{15}	$9514\ 820_{1903}$
·414	$9299\ 250_{3082}$	6623_{15}	$9604\ 716_{1766}$	·464	$9139\ 608_{3302}$	5888_{15}	$9512\ 917_{1906}$
0·415	$9296\ 168_{3087}$	6608_{14}	$9602\ 950_{1769}$	**0·465**	$9136\ 306_{3306}$	5873_{15}	$9511\ 011_{1909}$
·416	$9293\ 081_{3091}$	6594_{14}	$9601\ 181_{1772}$	·466	$9133\ 000_{3310}$	5858_{15}	$9509\ 102_{1911}$
·417	$9289\ 990_{3097}$	6580_{15}	$9599\ 409_{1775}$	·467	$9129\ 690_{3313}$	5842_{16}	$9507\ 191_{1913}$
·418	$9286\ 893_{3100}$	6565_{14}	$9597\ 634_{1777}$	·468	$9126\ 377_{3318}$	5827_{15}	$9505\ 278_{1916}$
·419	$9283\ 793_{3106}$	6551_{14}	$9595\ 857_{1781}$	·469	$9123\ 059_{3322}$	5812_{15}	$9503\ 362_{1919}$
0·420	$9280\ 687_{3110}$	6537_{15}	$9594\ 076_{1784}$	**0·470**	$9119\ 737_{3326}$	5797_{15}	$9501\ 443_{1921}$
·421	$9277\ 577_{3115}$	6522_{14}	$9592\ 292_{1786}$	·471	$9116\ 411_{3329}$	5782_{15}	$9499\ 522_{1924}$
·422	$9274\ 462_{3120}$	6508_{15}	$9590\ 506_{1790}$	·472	$9113\ 082_{3334}$	5767_{15}	$9497\ 598_{1927}$
·423	$9271\ 342_{3125}$	6493_{14}	$9588\ 716_{1792}$	·473	$9109\ 748_{3337}$	5752_{16}	$9495\ 671_{1929}$
·424	$9268\ 217_{3128}$	6479_{15}	$9586\ 924_{1796}$	·474	$9106\ 411_{3341}$	5736_{15}	$9493\ 742_{1931}$
0·425	$9265\ 089_{3134}$	6464_{14}	$9585\ 128_{1798}$	**0·475**	$9103\ 070_{3345}$	5721_{15}	$9491\ 811_{1934}$
·426	$9261\ 955_{3138}$	6450_{15}	$9583\ 330_{1801}$	·476	$9099\ 725_{3349}$	5706_{15}	$9489\ 877_{1937}$
·427	$9258\ 817_{3143}$	6435_{14}	$9581\ 529_{1804}$	·477	$9096\ 376_{3353}$	5691_{15}	$9487\ 940_{1939}$
·428	$9255\ 674_{3147}$	6421_{15}	$9579\ 725_{1807}$	·478	$9093\ 023_{3356}$	5676_{16}	$9486\ 001_{1941}$
·429	$9252\ 527_{3152}$	6406_{14}	$9577\ 918_{1810}$	·479	$9089\ 667_{3361}$	5660_{15}	$9484\ 060_{1945}$
0·430	$9249\ 375_{3157}$	6392_{15}	$9576\ 108_{1812}$	**0·480**	$9086\ 306_{3364}$	5645_{15}	$9482\ 115_{1946}$
·431	$9246\ 218_{3161}$	6377_{14}	$9574\ 296_{1816}$	·481	$9082\ 942_{3368}$	5630_{16}	$9480\ 169_{1949}$
·432	$9243\ 057_{3165}$	6363_{15}	$9572\ 480_{1818}$	·482	$9079\ 574_{3371}$	5614_{15}	$9478\ 220_{1952}$
·433	$9239\ 892_{3170}$	6348_{15}	$9570\ 662_{1822}$	·483	$9076\ 203_{3376}$	5599_{15}	$9476\ 268_{1954}$
·434	$9236\ 722_{3175}$	6333_{14}	$9568\ 840_{1824}$	·484	$9072\ 827_{3379}$	5584_{15}	$9474\ 314_{1956}$
0·435	$9233\ 547_{3179}$	6319_{15}	$9567\ 016_{1827}$	**0·485**	$9069\ 448_{3383}$	5569_{16}	$9472\ 358_{1959}$
·436	$9230\ 368_{3183}$	6304_{15}	$9565\ 189_{1829}$	·486	$9066\ 065_{3386}$	5553_{15}	$9470\ 399_{1962}$
·437	$9227\ 185_{3188}$	6289_{14}	$9563\ 360_{1833}$	·487	$9062\ 679_{3391}$	5538_{15}	$9468\ 437_{1964}$
·438	$9223\ 997_{3192}$	6275_{15}	$9561\ 527_{1835}$	·488	$9059\ 288_{3393}$	5523_{15}	$9466\ 473_{1966}$
·439	$9220\ 805_{3197}$	6260_{15}	$9559\ 692_{1838}$	·489	$9055\ 895_{3398}$	5507_{15}	$9464\ 507_{1969}$
0·440	$9217\ 608_{3201}$	6245_{14}	$9557\ 854_{1841}$	**0·490**	$9052\ 497_{3401}$	5492_{16}	$9462\ 538_{1971}$
·441	$9214\ 407_{3205}$	6231_{14}	$9556\ 013_{1844}$	·491	$9049\ 096_{3405}$	5476_{15}	$9460\ 567_{1973}$
·442	$9211\ 202_{3210}$	6216_{15}	$9554\ 169_{1847}$	·492	$9045\ 691_{3408}$	5461_{15}	$9458\ 594_{1976}$
·443	$9207\ 992_{3214}$	6201_{15}	$9552\ 322_{1849}$	·493	$9042\ 283_{3412}$	5446_{15}	$9456\ 618_{1979}$
·444	$9204\ 778_{3218}$	$·6186_{14}$	$9550\ 473_{1852}$	·494	$9038\ 871_{3416}$	5430_{15}	$9454\ 639_{1980}$
0·445	$9201\ 560_{3223}$	6172_{15}	$9548\ 621_{1855}$	**0·495**	$9035\ 455_{3419}$	5415_{16}	$9452\ 659_{1984}$
·446	$9198\ 337_{3227}$	6157_{15}	$9546\ 766_{1857}$	·496	$9032\ 036_{3423}$	5399_{16}	$9450\ 675_{1985}$
·447	$9195\ 110_{3231}$	6142_{15}	$9544\ 909_{1861}$	·497	$9028\ 613_{3426}$	5384_{15}	$9448\ 690_{1988}$
·448	$9191\ 879_{3236}$	6127_{15}	$9543\ 048_{1863}$	·498	$9025\ 187_{3430}$	5368_{15}	$9446\ 702_{1990}$
·449	$9188\ 643_{3240}$	6112_{15}	$9541\ 185_{1865}$	·499	$9021\ 757_{3433}$	5353_{16}	$9444\ 712_{1993}$
0·450	$9185\ 403$	6097	$9539\ 320$	**0·500**	$9018\ 324$	5337	$9442\ 719$

TABLE 1.

$\alpha^{\frac12}\mu$	A	I	N	$\alpha^{\frac12}\mu$	A	I	N
	0·	2·	0·		0·	2·	0·
0·500	9018 324$_{3437}$	5337$_{15}$	9442 719$_{1995}$	0·550	8842 513$_{3593}$	4552$_{16}$	9340 246$_{2103}$
·501	9014 887$_{3440}$	5322$_{16}$	9440 724$_{1997}$	·551	8838 920$_{3595}$	4536$_{16}$	9338 143$_{2105}$
·502	9011 447$_{3444}$	5306$_{15}$	9438 727$_{2000}$	·552	8835 325$_{3599}$	4520$_{15}$	9336 038$_{2107}$
·503	9008 003$_{3447}$	5291$_{16}$	9436 727$_{2002}$	·553	8831 726$_{3601}$	4505$_{16}$	9333 931$_{2109}$
·504	9004 556$_{3450}$	5275$_{15}$	9434 725$_{2004}$	·554	8828 125$_{3604}$	4489$_{16}$	9331 822$_{2111}$
0·505	9001 106$_{3454}$	5260$_{16}$	9432 721$_{2007}$	0·555	8824 521$_{3606}$	4473$_{16}$	9329 711$_{2113}$
·506	8997 652$_{3458}$	5244$_{15}$	9430 714$_{2009}$	·556	8820 915$_{3610}$	4457$_{16}$	9327 598$_{2115}$
·507	8994 194$_{3460}$	5229$_{16}$	9428 705$_{2011}$	·557	8817 305$_{3612}$	4441$_{16}$	9325 483$_{2117}$
·508	8990 734$_{3465}$	5213$_{15}$	9426 694$_{2013}$	·558	8813 693$_{3614}$	4425$_{16}$	9323 366$_{2119}$
·509	8987 269$_{3467}$	5198$_{16}$	9424 681$_{2016}$	·559	8810 079$_{3617}$	4409$_{16}$	9321 247$_{2121}$
0·510	8983 802$_{3471}$	5182$_{15}$	9422 665$_{2018}$	0·560	8806 462$_{3620}$	4393$_{16}$	9319 126$_{2122}$
·511	8980 331$_{3474}$	5167$_{16}$	9420 647$_{2020}$	·561	8802 842$_{3623}$	4377$_{16}$	9317 004$_{2125}$
·512	8976 857$_{3478}$	5151$_{16}$	9418 627$_{2023}$	·562	8799 219$_{3625}$	4361$_{16}$	9314 879$_{2126}$
·513	8973 379$_{3480}$	5135$_{15}$	9416 604$_{2025}$	·563	8795 594$_{3628}$	4345$_{16}$	9312 753$_{2128}$
·514	8969 899$_{3484}$	5120$_{16}$	9414 579$_{2027}$	·564	8791 966$_{3630}$	4329$_{16}$	9310 625$_{2131}$
0·515	8966 415$_{3488}$	5104$_{16}$	9412 552$_{2029}$	0·565	8788 336$_{3633}$	4313$_{16}$	9308 494$_{2132}$
·516	8962 927$_{3490}$	5088$_{15}$	9410 523$_{2032}$	·566	8784 703$_{3635}$	4297$_{16}$	9306 362$_{2134}$
·517	8959 437$_{3494}$	5073$_{16}$	9408 491$_{2033}$	·567	8781 068$_{3638}$	4281$_{16}$	9304 228$_{2136}$
·518	8955 943$_{3497}$	5057$_{15}$	9406 458$_{2036}$	·568	8777 430$_{3641}$	4265$_{16}$	9302 092$_{2137}$
·519	8952 446$_{3500}$	5042$_{16}$	9404 422$_{2039}$	·569	8773 789$_{3643}$	4249$_{16}$	9299 955$_{2140}$
0·520	8948 946$_{3504}$	5026$_{16}$	9402 383$_{2040}$	0·570	8770 146$_{3645}$	4233$_{16}$	9297 815$_{2141}$
·521	8945 442$_{3507}$	5010$_{16}$	9400 343$_{2043}$	·571	8766 501$_{3648}$	4217$_{16}$	9295 674$_{2144}$
·522	8941 935$_{3509}$	4994$_{15}$	9398 300$_{2044}$	·572	8762 853$_{3651}$	4201$_{16}$	9293 530$_{2145}$
·523	8938 426$_{3513}$	4979$_{16}$	9396 256$_{2047}$	·573	8759 202$_{3653}$	4185$_{16}$	9291 385$_{2147}$
·524	8934 913$_{3517}$	4963$_{16}$	9394 209$_{2049}$	·574	8755 549$_{3655}$	4169$_{16}$	9289 238$_{2148}$
0·525	8931 396$_{3519}$	4947$_{15}$	9392 160$_{2052}$	0·575	8751 894$_{3658}$	4153$_{16}$	9287 090$_{2151}$
·526	8927 877$_{3522}$	4932$_{16}$	9390 108$_{2053}$	·576	8748 236$_{3660}$	4137$_{16}$	9284 939$_{2152}$
·527	8924 355$_{3526}$	4916$_{16}$	9388 055$_{2056}$	·577	8744 576$_{3663}$	4121$_{16}$	9282 787$_{2155}$
·528	8920 829$_{3528}$	4900$_{16}$	9385 999$_{2057}$	·578	8740 913$_{3665}$	4105$_{16}$	9280 632$_{2156}$
·529	8917 301$_{3532}$	4884$_{15}$	9383 942$_{2060}$	·579	8737 248$_{3668}$	4089$_{16}$	9278 476$_{2157}$
0·530	8913 769$_{3535}$	4869$_{16}$	9381 882$_{2062}$	0·580	8733 580$_{3670}$	4073$_{16}$	9276 319$_{2160}$
·531	8910 234$_{3537}$	4853$_{16}$	9379 820$_{2065}$	·581	8729 910$_{3672}$	4057$_{16}$	9274 159$_{2161}$
·532	8906 697$_{3541}$	4837$_{16}$	9377 755$_{2066}$	·582	8726 238$_{3674}$	4041$_{16}$	9271 998$_{2163}$
·533	8903 156$_{3544}$	4821$_{15}$	9375 689$_{2068}$	·583	8722 564$_{3677}$	4025$_{16}$	9269 835$_{2165}$
·534	8899 612$_{3547}$	4806$_{16}$	9373 621$_{2071}$	·584	8718 887$_{3679}$	4009$_{16}$	9267 670$_{2167}$
0·535	8896 065$_{3549}$	4790$_{16}$	9371 550$_{2072}$	0·585	8715 208$_{3682}$	3993$_{16}$	9265 503$_{2168}$
·536	8892 516$_{3553}$	4774$_{16}$	9369 478$_{2075}$	·586	8711 526$_{3684}$	3977$_{17}$	9263 335$_{2170}$
·537	8888 963$_{3556}$	4758$_{16}$	9367 403$_{2077}$	·587	8707 842$_{3686}$	3960$_{16}$	9261 165$_{2172}$
·538	8885 407$_{3559}$	4742$_{15}$	9365 326$_{2078}$	·588	8704 156$_{3688}$	3944$_{16}$	9258 993$_{2173}$
·539	8881 848$_{3561}$	4727$_{16}$	9363 248$_{2081}$	·589	8700 468$_{3691}$	3928$_{16}$	9256 820$_{2176}$
0·540	8878 287$_{3565}$	4711$_{16}$	9361 167$_{2083}$	0·590	8696 777$_{3693}$	3912$_{16}$	9254 644$_{2177}$
·541	8874 722$_{3567}$	4695$_{16}$	9359 084$_{2085}$	·591	8693 084$_{3695}$	3896$_{16}$	9252 467$_{2178}$
·542	8871 155$_{3570}$	4679$_{16}$	9356 999$_{2087}$	·592	8689 389$_{3697}$	3880$_{16}$	9250 289$_{2181}$
·543	8867 585$_{3573}$	4663$_{16}$	9354 912$_{2089}$	·593	8685 692$_{3699}$	3864$_{16}$	9248 108$_{2182}$
·544	8864 012$_{3576}$	4647$_{15}$	9352 823$_{2091}$	·594	8681 993$_{3702}$	3848$_{16}$	9245 926$_{2183}$
0·545	8860 436$_{3579}$	4632$_{16}$	9350 732$_{2093}$	0·595	8678 291$_{3704}$	3832$_{16}$	9243 743$_{2186}$
·546	8856 857$_{3582}$	4616$_{16}$	9348 639$_{2096}$	·596	8674 587$_{3706}$	3816$_{16}$	9241 557$_{2187}$
·547	8853 275$_{3584}$	4600$_{16}$	9346 543$_{2097}$	·597	8670 881$_{3708}$	3800$_{17}$	9239 370$_{2189}$
·548	8849 691$_{3588}$	4584$_{16}$	9344 446$_{2099}$	·598	8667 173$_{3710}$	3783$_{16}$	9237 181$_{2190}$
·549	8846 103$_{3590}$	4568$_{16}$	9342 347$_{2101}$	·599	8663 463$_{3713}$	3767$_{16}$	9234 991$_{2192}$
0·550	8842 513	4552	9340 246	0·600	8659 750	3751	9232 799

TABLE 2.

α	c	h	α	c	h
0·000	1·000 0000 ₍3999₎	0·00000 ₍100₎	**0·050**	1·019 7631 ₍3905₎	0·04860 ₍95₎
·001	·000 3999 ₍3997₎	·00100 ₍100₎	·051	·020 1536 ₍3904₎	·04955 ₍94₎
·002	·000 7996 ₍3995₎	·00200 ₍100₎	·052	·020 5440 ₍3902₎	·05049 ₍94₎
·003	·001 1991 ₍3993₎	·00299 ₍99₎	·053	·020 9342 ₍3900₎	·05143 ₍94₎
·004	·001 5984 ₍3992₎	·00399 ₍100₎	·054	·021 3242 ₍3898₎	·05237 ₍94₎
0·005	1·001 9976 ₍3989₎	0·00499 ₍99₎	**0·055**	1·021 7140 ₍3896₎	0·05331 ₍94₎
·006	·002 3965 ₍3988₎	·00598 ₍99₎	·056	·022 1036 ₍3895₎	·05425 ₍94₎
·007	·002 7953 ₍3985₎	·00697 ₍99₎	·057	·022 4931 ₍3893₎	·05519 ₍94₎
·008	·003 1938 ₍3984₎	·00796 ₍99₎	·058	·022 8824 ₍3891₎	·05613 ₍93₎
·009	·003 5922 ₍3981₎	·00895 ₍99₎	·059	·023 2715 ₍3889₎	·05706 ₍94₎
0·010	1·003 9903 ₍3980₎	0·00994 ₍99₎	**0·060**	1·023 6604 ₍3888₎	0·05800 ₍93₎
·011	·004 3883 ₍3978₎	·01093 ₍99₎	·061	·024 0492 ₍3886₎	·05893 ₍93₎
·012	·004 7861 ₍3976₎	·01192 ₍98₎	·062	·024 4378 ₍3884₎	·05986 ₍94₎
·013	·005 1837 ₍3974₎	·01290 ₍99₎	·063	·024 8262 ₍3882₎	·06080 ₍93₎
·014	·005 5811 ₍3972₎	·01389 ₍98₎	·064	·025 2144 ₍3880₎	·06173 ₍93₎
0·015	1·005 9783 ₍3970₎	0·01487 ₍98₎	**0·065**	1·025 6024 ₍3879₎	0·06266 ₍93₎
016	·006 3753 ₍3969₎	·01585 ₍98₎	·066	·025 9903 ₍3877₎	·06359 ₍92₎
·017	·006 7722 ₍3966₎	·01683 ₍99₎	·067	·026 3780 ₍3875₎	·06451 ₍93₎
·018	·007 1688 ₍3965₎	·01782 ₍97₎	·068	·026 7655 ₍3874₎	·06544 ₍93₎
·019	·007 5653 ₍3962₎	·01879 ₍98₎	·069	·027 1529 ₍3871₎	·06637 ₍92₎
0·020	1·007 9615 ₍3961₎	0·01977 ₍98₎	**0·070**	1·027 5400 ₍3870₎	0·06729 ₍92₎
·021	·008 3576 ₍3959₎	·02075 ₍97₎	·071	·027 9270 ₍3868₎	·06821 ₍93₎
·022	·008 7535 ₍3957₎	·02172 ₍98₎	·072	·028 3138 ₍3867₎	·06914 ₍92₎
·023	·009 1492 ₍3955₎	·02270 ₍97₎	·073	·028 7005 ₍3864₎	·07006 ₍92₎
·024	·009 5447 ₍3953₎	·02367 ₍97₎	·074	·029 0869 ₍3863₎	·07098 ₍92₎
0·025	1·009 9400 ₍3952₎	0·02464 ₍98₎	**0·075**	1·029 4732 ₍3861₎	0·07190 ₍92₎
·026	·010 3352 ₍3949₎	·02562 ₍97₎	·076	·029 8593 ₍3860₎	·07282 ₍91₎
·027	·010 7301 ₍3948₎	·02659 ₍97₎	·077	·030 2453 ₍3857₎	·07373 ₍92₎
·028	·011 1249 ₍3946₎	·02756 ₍96₎	·078	·030 6310 ₍3856₎	·07465 ₍92₎
·029	·011 5195 ₍3944₎	·02852 ₍97₎	·079	·031 0166 ₍3855₎	·07557 ₍91₎
0·030	1·011 9139 ₍3942₎	0·02949 ₍97₎	**0·080**	1·031 4021 ₍3852₎	0·07648 ₍91₎
·031	·012 3081 ₍3940₎	·03046 ₍96₎	·081	·031 7873 ₍3851₎	·07739 ₍92₎
·032	·012 7021 ₍3938₎	·03142 ₍96₎	·082	·032 1724 ₍3849₎	·07831 ₍91₎
·033	·013 0959 ₍3937₎	·03238 ₍97₎	·083	·032 5573 ₍3847₎	·07922 ₍91₎
·034	·013 4896 ₍3934₎	·03335 ₍96₎	·084	·032 9420 ₍3846₎	·08013 ₍91₎
0·035	1·013 8830 ₍3933₎	0·03431 ₍96₎	**0·085**	1·033 3266 ₍3844₎	0·08104 ₍91₎
·036	·014 2763 ₍3931₎	·03527 ₍96₎	·086	·033 7110 ₍3842₎	·08195 ₍91₎
·037	·014 6694 ₍3929₎	·03623 ₍96₎	·087	·034 0952 ₍3840₎	·08285 ₍91₎
·038	·015 0623 ₍3928₎	·03719 ₍95₎	·088	·034 4792 ₍3839₎	·08376 ₍91₎
·039	·015 4551 ₍3925₎	·03814 ₍96₎	·089	·034 8631 ₍3837₎	·08467 ₍90₎
0·040	1·015 8476 ₍3924₎	0·03910 ₍95₎	**0·090**	1·035 2468 ₍3835₎	0·08557 ₍90₎
·041	·016 2400 ₍3922₎	·04005 ₍96₎	·091	·035 6303 ₍3834₎	·08647 ₍91₎
·042	·016 6322 ₍3920₎	·04101 ₍95₎	·092	·036 0137 ₍3832₎	·08738 ₍90₎
·043	·017 0242 ₍3918₎	·04196 ₍95₎	·093	·036 3969 ₍3830₎	·08828 ₍90₎
·044	·017 4160 ₍3916₎	·04291 ₍95₎	·094	·036 7799 ₍3828₎	·08918 ₍90₎
0·045	1·017 8076 ₍3915₎	0·04386 ₍95₎	**0·095**	1·037 1627 ₍3827₎	0·09008 ₍89₎
·046	·018 1991 ₍3912₎	·04481 ₍95₎	·096	·037 5454 ₍3825₎	·09097 ₍90₎
·047	·018 5903 ₍3911₎	·04576 ₍95₎	·097	·037 9279 ₍3824₎	·09187 ₍90₎
·048	·018 9814 ₍3911₎	·04671 ₍95₎	·098	·038 3103 ₍3824₎	·09277 ₍90₎
·049	·019 3723 ₍3909₎ ₍3908₎	·04766 ₍95₎ ₍94₎	·099	·038 6924 ₍3821₎ ₍3821₎	·09366 ₍89₎ ₍90₎
0·050	1·019 7631	0·04860	**0·100**	1·039 0745	0·09456

TABLE 3.

$\alpha^{\frac{1}{2}}\sigma$	J	K	$\alpha^{\frac{1}{2}}\sigma$	J	K
0·000	1·000 0000	0·000 0000$_0$	**0·050**	1·000 ·3750$_{152}$	0·000 0072$_2$
·001	·000 0002$_2$	0000^0	**·051**	·000 3902$_{154}$	0074^2
·002	·000 0006$_4$	0000^0	**·052**	·000 4056$_{158}$	·0077^3
·003	·000 0014$_8$	0000^0	**·053**	·000 4214$_{160}$	0080^3
·004	·000 0024$_{10}$	0000^1	**·054**	·000 4374$_{164}$	0083$^3_4$
0·005	1·000 0038$_{16}$	0·000 0001^0	**0·055**	1·000 4538$_{166}$	0·000 0087^3
·006	·000 0054$_{20}$	0001^0	**·056**	·000 4704$_{170}$	0090^3
·007	·000 0074$_{22}$	0001^0	**·057**	·000 4874$_{172}$	0093^3
·008	·000 0096$_{26}$	0002^1	**·058**	·000 5046$_{176}$	0096^3
·009	·000 0122$_{28}$	0002^1	**·059**	·000 5222$_{178}$	0100$^4_3$
0·010	1·000 0150$_{32}$	0·000 0003^0	**0·060**	1·000 5400$_{182}$	0·000 0103^3
·011	·000 0182$_{34}$	0003^0	**·061**	·000 5582$_{184}$	0106^3
·012	·000 0216$_{38}$	0004^1	**·062**	·000 5766$_{188}$	0110^4
·013	·000 0254$_{40}$	0005^1	**·063**	·000 5954$_{190}$	0114$^3_4$
·014	·000 0294$_{44}$	0006$^1_0$	**·064**	·000 6144$_{194}$	0117$^3_4$
0·015	1·000 0338$_{46}$	0·000 0006^1	**0·065**	1·000 6338$_{196}$	0·000 0121^4
·016	·000 0384$_{50}$	0007^1	**·066**	·000 6534$_{200}$	0125^4
·017	·000 0434$_{52}$	0008^1	**·067**	·000 6734$_{202}$	0128^3
·018	·000 0486$_{56}$	0009^1	**·068**	·000 6936$_{206}$	0132^4
·019	·000 0542$_{58}$	0010$^1_1$	**·069**	·000 7142$_{208}$	0136$^4_4$
0·020	1·000 0600$_{62}$	0·000 0011^2	**0·070**	1·000 7350$_{212}$	0·000 0140^4
·021	·000 0662$_{64}$	0013^1	**·071**	·000 7562$_{214}$	0144^4
·022	·000 0726$_{68}$	0014^1	**·072**	·000 7776$_{218}$	0148^4
·023	·000 0794$_{70}$	0015^1	**·073**	·000 7994$_{220}$	0153^5
·024	·000 0864$_{74}$	0016$^1_2$	**·074**	·000 8214$_{224}$	0157^4
0·025	1·000 0938$_{76}$	0·000 0018^2	**0·075**	1·000 8438$_{226}$	0·000 0161^4
·026	·000 1014$_{80}$	0019^1	**·076**	·000 8664$_{230}$	0165^4
·027	·000 1094$_{82}$	0021^2	**·077**	·000 8894$_{232}$	0170^5
·028	·000 1176$_{86}$	0022^1	**·078**	·000 9126$_{236}$	0174^4
·029	·000 1262$_{88}$	0024$^2_2$	**·079**	·000 9362$_{238}$	0179$^5_4$
0·030	1·000 1350$_{92}$	0·000 0026^1	**0·080**	1·000 9600$_{242}$	0·000 0183^5
·031	·000 1442$_{94}$	0027^1	**·081**	·000 9842$_{244}$	0188^5
·032	·000 1536$_{98}$	0029^2	**·082**	·001 0086$_{248}$	0193^5
·033	·000 1634$_{100}$	0031^2	**·083**	·001 0334$_{250}$	0197^4
·034	·000 1734$_{104}$	0033$^2_2$	**·084**	·001 0584$_{254}$	0202$^5_5$
0·035	1·000 1838$_{106}$	0·000 0035^2	**0·085**	1·001 0838$_{256}$	0·000 0207^5
·036	·000 1944$_{110}$	·0037^2	**·086**	·001 1094$_{260}$	0212^5
·037	·000 2054$_{112}$	0039^2	**·087**	·001 1354$_{262}$	0217^5
·038	·000 2166$_{116}$	0041^2	**·088**	·001 1616$_{266}$	0222^5
·039	·000 2282$_{118}$	0043$^2_3$	**·089**	·001 1882$_{268}$	0227$^5_5$
0·040	1·000 2400$_{122}$	0·000 0046^2	**0·090**	1·001 2150$_{272}$	0·000 0232^5
·041	·000 2522$_{124}$	0048^2	**·091**	·001 2422$_{275}$	0237^5
·042	·000 2646$_{128}$	0050^2	**·092**	·001 2697$_{277}$	0243^6
·043	·000 2774$_{130}$	0053^3	**·093**	·001 2974$_{281}$	0248^5
·044	·000 2904$_{134}$	0055$^2_3$	**·094**	·001 3255$_{283}$	0253$^5_6$
0·045	1·000 3038$_{136}$	0·000 0058^3	**0·095**	1·001 3538$_{287}$	0·000 0259^5
·046	·000 3174$_{140}$	0061^3	**·096**	·001 3825$_{289}$	0264^6
·047	·000 3314$_{142}$	0063^2	**·097**	·001 4114$_{293}$	0270^5
·048	·000 3456$_{146}$	0066^3	**·098**	·001 4407$_{295}$	0275^6
·049	·000 3602$_{148}$	0069$^3_3$	**·099**	·001 4702$_{299}$	0281$^6_6$
0·050	1·000 3750	0·000 0072	**0·100**	1·001 ·5001	0·000 0287

TABLE 3.

$\alpha^{\frac{1}{2}}\sigma$	J	K	$\alpha^{\frac{1}{2}}\sigma$	J	K
0·100	1·001 5001	0·000 0287$_6$	**0·150**	1·003 3754^{451}	0·000 0649$_8$
·101	·001 5302^{301}	0293$_5$	·151	·003 4205^{455}	0657$_8$
·102	·001 5607^{305}	0298$_5$	·152	·003 4660^{457}	0666$_9$
·103	·001 5914^{307}	0304$_6$	·153	·003 5117^{461}	0675$_9$
·104	·001 6225$^{311}_{313}$	0310$_6$	·154	·003 5578$^{461}_{464}$	0684$_9$
0·105	1·001 6538^{317}	0·000 0316$_6$	**0·155**	1·003 6042^{466}	0·000 0693$_9$
·106	·001 6855^{317}	0322$_6$	·156	·003 6508^{470}	0702$_9$
·107	·001 7174^{319}	0329$_7$	·157	·003 6978^{472}	0711$_9$
·108	·001 7497^{323}	0335$_6$	·158	·003 7450^{476}	0720$_{10}$
·109	·001 7822$^{325}_{329}$	0341$_6$	·159	·003 7926$^{476}_{479}$	0730$_9$
0·110	1·001 8151^{332}	0·000 0347$_7$	**0·160**	1·003 8405^{481}	0·000 0739$_9$
·111	·001 8483^{332}	0354$_6$	·161	·003 8886^{485}	0748$_{10}$
·112	·001 8817^{334}	0360$_6$	·162	·003 9371^{488}	0758$_9$
·113	·001 9155^{338}	0367$_7$	·163	·003 9859^{490}	0767$_{10}$
·114	·001 9495$^{340}_{344}$	0373$_6$	·164	·004 0349$^{490}_{494}$	0777$_9$
0·115	1·001 9839^{346}	0·000 0380$_6$	**0·165**	1·004 0843^{496}	0·000 0786$_{10}$
·116	·002 0185^{346}	0386$_6$	·166	·004 1339^{496}	0796$_{10}$
·117	·002 0535^{350}	0393$_7$	·167	·004 1839^{500}	0806$_9$
·118	·002 0887^{352}	0400$_7$	·168	·004 2342^{503}	0815$_{10}$
·119	·002 1243$^{356}_{358}$	0407$_7$	·169	·004 2847$^{505}_{509}$	0825$_{10}$
0·120	1·002 1601^{358}	0·000 0414$_7$	**0·170**	1·004 3356^{512}	0·000 0835$_{10}$
·121	·002 1963^{362}	0421$_7$	·171	·004 3868^{512}	0845$_{10}$
·122	·002 2328^{365}	0428$_7$	·172	·004 4382^{514}	0855$_{10}$
·123	·002 2695^{367}	0435$_7$	·173	·004 4900^{518}	0865$_{10}$
·124	·002 3066$^{371}_{373}$	0442$_7$	·174	·004 5421$^{521}_{523}$	0875$_{11}$
0·125	1·002 3439^{377}	0·000 0449$_7$	**0·175**	1·004 5944^{527}	0·000 0886$_{10}$
·126	·002 3816^{377}	0456$_7$	·176	·004 6471^{527}	0896$_{10}$
·127	·002 4195^{379}	0464$_8$	·177	·004 7000^{529}	0906$_{11}$
·128	·002 4578^{383}	0471$_7$	·178	·004 7533^{533}	0917$_{10}$
·129	·002 4963$^{385}_{389}$	0479$_8$	·179	·004 8069$^{536}_{538}$	0927$_{11}$
0·130	1·002 5352^{392}	0·000 0486$_8$	**0·180**	1·004 8607^{542}	0·000 0938$_{10}$
·131	·002 5744^{392}	0494$_7$	·181	·004 9149^{542}	0948$_{10}$
·132	·002 6138^{394}	0501$_8$	·182	·004 9694^{545}	0959$_{11}$
·133	·002 6536^{398}	0509$_8$	·183	·005 0242^{548}	0969$_{10}$
·134	·002 6936$^{400}_{404}$	0517$_7$	·184	·005 0792$^{550}_{554}$	0980$_{11}$
0·135	1·002 7340^{406}	0·000 0524$_8$	**0·185**	1·005 1346^{557}	0·000 0991$_{11}$
·136	·002 7746^{406}	0532$_8$	·186	·005 1903^{557}	1002$_{11}$
·137	·002 8156^{410}	0540$_8$	·187	·005 2462^{559}	1013$_{11}$
·138	·002 8569^{413}	0548$_8$	·188	·005 3025^{563}	1024$_{11}$
·139	·002 8984$^{415}_{419}$	0556$_8$	·189	·005 3591$^{566}_{568}$	1035$_{11}$
0·140	1·002 9403^{421}	0·000 0564$_8$	**0·190**	1·005 4159^{572}	0·000 1046$_{11}$
·141	·002 9824^{421}	0572$_8$	·191	·005 4731^{572}	1057$_{12}$
·142	·003 0249^{425}	0581$_9$	·192	·005 5306^{575}	1069$_{11}$
·143	·003 0676^{427}	0589$_8$	·193	·005 5883^{577}	1080$_{11}$
·144	·003 1107$^{431}_{434}$	0597$_9$	·194	·005 6464$^{581}_{584}$	1091$_{12}$
0·145	1·003 1541^{436}	0·000 0606$_8$	**0·195**	1·005 7048^{587}	0·000 1103$_{11}$
·146	·003 1977^{436}	0614$_9$	·196	·005 7635^{587}	1114$_{12}$
·147	·003 2417^{440}	0623$_8$	·197	·005 8224^{589}	1126$_{11}$
·148	·003 2859^{442}	0631$_9$	·198	·005 8817^{593}	1137$_{12}$
·149	·003 3305$^{446}_{449}$	0640$_9$	·199	·005 9413$^{596}_{598}$	1149$_{12}$
0·150	1·003 3754	0·000 0649	**0·200**	1·006 0011	0·000 1161

TABLE 3.

$\alpha^{\frac12}\sigma$	J	K	$\alpha^{\frac12}\sigma$	J	K
0·200	$1{\cdot}006\ 0011_{602}$	$0{\cdot}000\ 1161_{12}$	0·250	$1{\cdot}009\ 3778_{752}$	$0{\cdot}000\ 1830_{15}$
·201	$\cdot006\ 0613_{605}$	1173_{12}	·251	$\cdot009\ 4530_{755}$	1845_{15}
·202	$\cdot006\ 1218_{608}$	1185_{12}	·252	$\cdot009\ 5285_{758}$	1860_{15}
·203	$\cdot006\ 1826_{610}$	1196_{11}	·253	$\cdot009\ 6043_{761}$	1875_{15}
·204	$\cdot006\ 2436_{614}$	1209_{13}	·254	$\cdot009\ 6804_{764}$	1890_{15}
0·205	$1{\cdot}006\ 3050_{617}$	$0{\cdot}000\ 1221_{12}$	0·255	$1{\cdot}009\ 7568_{767}$	$0{\cdot}000\ 1905_{16}$
·206	$\cdot006\ 3667_{620}$	1233_{12}	·256	$\cdot009\ 8335_{770}$	1921_{15}
·207	$\cdot006\ 4287_{622}$	1245_{12}	·257	$\cdot009\ 9105_{773}$	1936_{15}
·208	$\cdot006\ 4909_{626}$	1257_{12}	·258	$\cdot009\ 9878_{776}$	1952_{16}
·209	$\cdot006\ 5535_{629}$	1269_{12}	·259	$\cdot010\ 0654_{779}$	1967_{15}
0·210	$1{\cdot}006\ 6164_{632}$	$0{\cdot}000\ 1282_{12}$	0·260	$1{\cdot}010\ 1433_{782}$	$0{\cdot}000\ 1983_{15}$
·211	$\cdot006\ 6796_{634}$	1294_{12}	·261	$\cdot010\ 2215_{785}$	1998_{15}
·212	$\cdot006\ 7430_{638}$	1307_{13}	·262	$\cdot010\ 3000_{788}$	2014_{16}
·213	$\cdot006\ 8068_{641}$	1319_{12}	·263	$\cdot010\ 3788_{791}$	2030_{16}
·214	$\cdot006\ 8709_{644}$	1332_{13}	·264	$\cdot010\ 4579_{794}$	2046_{16}
0·215	$1{\cdot}006\ 9353_{647}$	$0{\cdot}000\ 1345_{13}$	0·265	$1{\cdot}010\ 5373_{797}$	$0{\cdot}000\ 2062_{16}$
·216	$\cdot007\ 0000_{649}$	1358_{12}	·266	$\cdot010\ 6170_{800}$	2078_{16}
·217	$\cdot007\ 0649_{653}$	1370_{13}	·267	$\cdot010\ 6970_{803}$	2094_{16}
·218	$\cdot007\ 1302_{656}$	1383_{13}	·268	$\cdot010\ 7773_{806}$	2110_{16}
·219	$\cdot007\ 1958_{659}$	1396_{13}	·269	$\cdot010\ 8579_{809}$	2126_{17}
0·220	$1{\cdot}007\ 2617_{661}$	$0{\cdot}000\ 1409_{13}$	0·270	$1{\cdot}010\ 9388_{812}$	$0{\cdot}000\ 2143_{16}$
·221	$\cdot007\ 3278_{665}$	1422_{13}	·271	$\cdot011\ 0200_{815}$	2159_{16}
·222	$\cdot007\ 3943_{668}$	1435_{14}	·272	$\cdot011\ 1015_{818}$	2175_{16}
·223	$\cdot007\ 4611_{671}$	1449_{13}	·273	$\cdot011\ 1833_{821}$	2192_{17}
·224	$\cdot007\ 5282_{674}$	1462_{13}	·274	$\cdot011\ 2654_{824}$	2208_{16}
0·225	$1{\cdot}007\ 5956_{677}$	$0{\cdot}000\ 1475_{14}$	0·275	$1{\cdot}011\ 3478_{827}$	$0{\cdot}000\ 2225_{17}$
·226	$\cdot007\ 6633_{679}$	1489_{13}	·276	$\cdot011\ 4305_{830}$	2242_{17}
·227	$\cdot007\ 7312_{683}$	1502_{14}	·277	$\cdot011\ 5135_{833}$	2258_{16}
·228	$\cdot007\ 7995_{686}$	1516_{13}	·278	$\cdot011\ 5968_{837}$	2275_{17}
·229	$\cdot007\ 8681_{689}$	1529_{14}	·079	$\cdot011\ 6805_{839}$	2292_{17}
0·230	$1{\cdot}007\ 9370_{692}$	$0{\cdot}000\ 1543_{14}$	0·280	$1{\cdot}011\ 7644_{842}$	$0{\cdot}000\ 2309_{17}$
·231	$\cdot008\ 0062_{695}$	1557_{13}	·281	$\cdot011\ 8486_{845}$	2326_{17}
·232	$\cdot008\ 0757_{697}$	1570_{14}	·282	$\cdot011\ 9331_{848}$	2343_{17}
·233	$\cdot008\ 1454_{701}$	1584_{14}	·283	$\cdot012\ 0179_{851}$	2360_{17}
·234	$\cdot008\ 2155_{704}$	1598_{14}	·284	$\cdot012\ 1030_{854}$	2378_{18}
0·235	$1{\cdot}008\ 2859_{707}$	$0{\cdot}000\ 1612_{14}$	0·285	$1{\cdot}012\ 1884_{858}$	$0{\cdot}000\ 2395_{17}$
·236	$\cdot008\ 3566_{710}$	1626_{14}	·286	$\cdot012\ 2742_{860}$	2412_{17}
·237	$\cdot008\ 4276_{713}$	1640_{14}	·287	$\cdot012\ 3602_{863}$	2430_{18}
·238	$\cdot008\ 4989_{716}$	1654_{15}	·288	$\cdot012\ 4465_{866}$	2447_{17}
·239	$\cdot008\ 5705_{719}$	1669_{14}	·289	$\cdot012\ 5331_{869}$	2465_{18}
0·240	$1{\cdot}008\ 6424_{722}$	$0{\cdot}000\ 1683_{14}$	0·290	$1{\cdot}012\ 6200_{872}$	$0{\cdot}000\ 2482_{18}$
·241	$\cdot008\ 7146_{724}$	1697_{15}	·291	$\cdot012\ 7072_{876}$	2500_{18}
·242	$\cdot008\ 7870_{728}$	1712_{14}	·292	$\cdot012\ 7948_{878}$	2518_{18}
·243	$\cdot008\ 8598_{731}$	1726_{15}	·293	$\cdot012\ 8826_{881}$	2536_{17}
·244	$\cdot008\ 9329_{734}$	1741_{14}	·294	$\cdot012\ 9707_{884}$	2553_{18}
0·245	$1{\cdot}009\ 0063_{737}$	$0{\cdot}000\ 1755_{15}$	0·295	$1{\cdot}013\ 0591_{888}$	$\cdot0000\ 2571_{18}$
·246	$\cdot009\ 0800_{740}$	1770_{15}	·296	$\cdot013\ 1479_{890}$	2589_{18}
·247	$\cdot009\ 1540_{743}$	1785_{15}	·297	$\cdot013\ 2369_{893}$	2608_{19}
·248	$\cdot009\ 2283_{746}$	1800_{15}	·298	$\cdot013\ 3262_{896}$	2626_{18}
·249	$\cdot009\ 3029_{749}$	1815_{15}	·299	$\cdot013\ 4158_{900}$	2644_{18}
0·250	$1{\cdot}009\ 3778$	$0{\cdot}000\ 1830$	0·300	$1{\cdot}013\ 5058$	$0{\cdot}000\ 2662$

TABLE 3.

$\alpha^{\frac12}\sigma$	J	K	$\alpha^{\frac12}\sigma$	J	K
0·300	1·013 5058	0·000 2662$_{19}$	**0·350**	1·018 3856^{1053}	0·000 3668$_{22}$
·301	·013 5960^{902}	2681$_{19}$	·351	·018 4909^{1056}	3690$_{22}$
·302	·013 6865^{905}	2699$_{18}$	·352	·018 5965^{1059}	3712$_{22}$
·303	·013 7773^{908}	2718$_{19}$	·353	·018 7024^{1061}	3734$_{22}$
·304	·013 8685$^{912}_{914}$	2736$_{18}^{19}$	·354	·018 8085^{1065}	3756$_{23}$
0·305	1·013 9599	0·000 2755$_{19}$	**0·355**	1·018 9150^{1068}	0·000 3779$_{22}$
·306	·014 0516^{917}	2774$_{19}$	·356	·019 0218^{1071}	3801$_{22}$
·307	·014 1437^{921}	2793$_{18}$	·357	·019 1289^{1073}	3823$_{22}$
·308	·014 2360^{923}	2811$_{19}$	·358	·019 2362^{1077}	3846$_{22}$
·309	·014 3286$^{926}_{930}$	2830$_{19}$	·359	·019 3439^{1080}	3868$_{23}$
0·310	1·014 4216	0·000 2849$_{19}$	**0·360**	1·019 4519^{1083}	0·000 3891$_{23}$
·311	·014 5148^{932}	2868$_{20}$	·361	·019 5602^{1086}	3914$_{22}$
·312	·014 6083^{935}	2888$_{19}$	·362	·019 6688^{1089}	3936$_{23}$
·313	·014 7022^{939}	2907$_{19}$	·363	·019 7777^{1091}	3950$_{23}$
·314	·014 7963$^{941}_{944}$	2926$_{19}$	·364	·019 8868^{1095}	3982$_{23}$
0·315	1·014 8907	0·000 2945$_{20}$	**0·365**	1·019 9963^{1098}	0·000 4005$_{23}$
·316	·014 9855^{948}	2965$_{19}$	·366	·020 1061^{1101}	4028$_{23}$
·317	·015 0805^{950}	2984$_{20}$	·367	·020 2162^{1104}	4051$_{24}$
·318	·015 1759^{954}	3004$_{20}$	·368	· 020 3266^{1107}	4075$_{24}$
·319	·015 2715$^{956}_{959}$	3024$_{19}$	·369	·020 4373^{1110}	4098$_{23}$
0·320	1·015 3674	0·000 3043$_{20}$	**0·370**	1·020 5483^{1113}	0·000 4121$_{24}$
·321	·015 4637^{963}	3063$_{20}$	·371	·020 6596^{1116}	4145$_{24}$
·322	·015 5602^{965}	3083$_{20}$	·372	·020 7712^{1119}	4168$_{23}$
·323	·015 6571^{969}	3103$_{20}$	·373	·020 8831^{1122}	4192$_{24}$
·324	·015 7542$^{971}_{975}$	3123$_{20}$	·374	·020 9953^{1125}	4216$_{23}$
0·325	1·015 8517	0·000 3143$_{20}$	**0·375**	1·021 1078^{1128}	0·000 4239$_{24}$
·326	·015 9494^{977}	3163$_{20}$	·376	·021 2206^{1131}	4263$_{24}$
·327	·016 0475^{981}	3183$_{21}$	·377	·021 3337^{1134}	4287$_{24}$
·328	·016 1458^{983}	3204$_{20}$	··378	·021 4471^{1137}	4311$_{24}$
·329	·016 2445$^{987}_{989}$	3224$_{20}$	·379	·021 5608^{1140}	4335$_{24}$
0·330	1·016 3434	0·000 3244$_{21}$	**0·380**	1·021 6748^{1143}	0·000 4359$_{24}$
·331	·016 4427^{993}	3265$_{20}$	·381	·021 7891^{1146}	4383$_{25}$
·332	·016 5422^{995}	3285$_{21}$	·382	·021 9037^{1149}	4408$_{24}$
·333	·016 6421^{999}	3306$_{21}$	·383	·022 0186^{1152}	4432$_{24}$
·334	·016 7422$^{1001}_{1005}$	3327$_{21}$	·384	·022 1338^{1155}	4456$_{25}$
0·335	1·016 8427	0·000 3348$_{20}$	**0·385**	1·022 2493^{1158}	0·000 4481$_{25}$
·336	·016 9434^{1007}	3368$_{21}$	·386	·022 3651^{1161}	4506$_{24}$
·337	·017 0445^{1011}	3389$_{21}$	·387	·022 4812^{1165}	4530$_{25}$
·338	·017 1459^{1014}	3410$_{21}$	·388	·022 5977^{1167}	4555$_{25}$
·339	·017 2475$^{1016}_{1020}$	3432$_{22}^{21}$	·389	·022 7144^{1170}	4580$_{25}$
0·340	1·017 3495	0·000 3453$_{21}$	**0·390**	1·022 8314^{1173}	0·000 4605$_{25}$
·341	·017 4517^{1022}	3474$_{21}$	·391	·022 9487^{1176}	4630$_{26}$
·342	·017 5543^{1026}	3495$_{22}$	·392	·023 0663^{1179}	4655$_{25}$
·343	·017 6572^{1029}	3517$_{22}$	·393	·023 1842^{1183}	4680$_{25}$
·344	·017 7603$^{1031}_{1035}$	3538$_{22}$	·394	·023 3025^{1185}	4705$_{25}$
0·345	1·017 8638	0·000 3560$_{21}$	**0·395**	1·023 4210^{1188}	0·000 4730$_{26}$
·346	·017 9676^{1038}	3581$_{22}$	·396	·023 5398^{1191}	4756$_{25}$
·347	·018 0716^{1040}	3603$_{21}$	·397	·023 6589^{1195}	4781$_{26}$
·348	·018 1760^{1044}	3624$_{22}$	·398	·023 7784^{1197}	4807$_{26}$
·349	·018 2807$^{1047}_{1049}$	3646$_{22}$	·399	·023 8981^{1200}	4832$_{26}$
0·350	1·018 3856	0·000 3668	**0·400**	1·024 0181	0·000 4858

TABLE 3.

$\alpha^{1}\sigma$	J	K	$\alpha^{1}\sigma$	J	K
0·400	1·024 0181$_{1204}$	0·000 4858$_{26}$	**0·450**	1·030 4040$_{1354}$	0·000 6244$_{29}$
·401	·024 1385$_{1206}$	4884$_{26}$	·451	·030 5394$_{1357}$	6273$_{30}$
·402	·024 2591$_{1209}$	4909$_{25}$	·452	·030 6751$_{1360}$	6303$_{30}$
·403	·024 3800$_{1213}$	4935$_{26}$	·453	·030 8111$_{1363}$	6333$_{30}$
·404	·024 5013$_{1215}$	4961$_{26}$	·454	·030 9474$_{1366}$	6363$_{30}$
0·405	1·024 6228	0·000 4987$_{27}$	**0·455**	1·031 0840$_{1369}$	0·000 6393$_{31}$
·406	·024 7446$_{1218}$	5014$_{27}$	·456	·031 2209$_{1372}$	6424$_{30}$
·407	·024 8668$_{1222}$	5040$_{26}$	·457	·031 3581$_{1376}$	6454$_{30}$
·408	·024 9892$_{1224}$	5066$_{26}$	·458	·031 4957$_{1378}$	6484$_{31}$
·409	·025 1120$_{1228}^{1230}$	5092$_{27}$	·459	·031 6335$_{1378}^{1381}$	6515$_{30}$
0·410	1·025 2350$_{1233}$	0·000 5119$_{26}$	**0·460**	1·031 7716$_{1384}$	0·000 6545$_{31}$
·411	·025 3583$_{1237}$	5145$_{27}$	·461	·031 9100$_{1388}$	6576$_{31}$
·412	·025 4820$_{1239}$	5172$_{27}$	·462	·032 0488$_{1390}$	6607$_{31}$
·413	·025 6059$_{1243}$	5199$_{27}$	·463	·032 1878$_{1393}$	6638$_{30}$
·414	·025 7302$_{1243}^{1245}$	5225$_{26}^{27}$	·464	·032 3271$_{1393}^{1397}$	6668$_{31}$
0·415	1·025 8547$_{1249}$	0·000 5252$_{27}$	**0·465**	1·032 4668$_{1399}$	0·000 6699$_{32}$
·416	·025 9796$_{1251}$	5279$_{27}$	·466	·032 6067$_{1402}$	6731$_{31}$
·417	·026 1047$_{1255}$	5306$_{27}$	·467	·032 7469$_{1406}$	6762$_{31}$
·418	·026 2302$_{1258}$	5333$_{27}$	·468	·032 8875$_{1408}$	6793$_{31}$
·419	·026 3560$_{1258}^{1260}$	5361$_{28}^{27}$	·469	·033 0283$_{1408}^{1411}$	6824$_{32}$
0·420	1·026 4820$_{1264}$	0·000 5388$_{27}$	**0·470**	1·033 1694$_{1415}$	0·000 6856$_{31}$
·421	·026 6084$_{1266}$	5415$_{27}$	·471	·033 3109$_{1417}$	6887$_{32}$
·422	·026 7350$_{1270}$	5443$_{28}$	·472	·033 4526$_{1421}$	6919$_{31}$
·423	·026 8620$_{1273}$	5470$_{27}$	·473	·033 5947$_{1423}$	6950$_{32}$
·424	·026 9893$_{1273}^{1275}$	5498$_{28}^{27}$	·474	·033 7370$_{1423}^{1427}$	6982$_{32}$
0·425	1·027 1168$_{1279}$	0·000 5525$_{28}$	**0·475**	1·033 8797$_{1429}$	0·000 7014$_{32}$
·426	·027 2447$_{1282}$	5553$_{28}$	·476	·034 0226$_{1433}$	7046$_{32}$
·427	·027 3729$_{1284}$	5581$_{28}$	·477	·034 1659$_{1435}$	7078$_{32}$
·428	·027 5013$_{1288}$	5609$_{28}$	·478	·034 3094$_{1439}$	7110$_{32}$
·429	·027 6301$_{1288}^{1291}$	5637$_{28}$	·479	·034 4533$_{1439}^{1441}$	7142$_{33}$
0·430	1·027 7592$_{1293}$	0·000 5665$_{28}$	**0·480**	1·034 5974$_{1445}$	0·000 7175$_{32}$
·431	·027 8885$_{1297}$	5693$_{28}$	·481	·034 7419$_{1448}$	7207$_{33}$
·432	·028 0182$_{1300}$	5721$_{29}$	·482	·034 8867$_{1450}$	7240$_{32}$
·433	·028 1482$_{1303}$	5750$_{28}$	·483	·035 0317$_{1454}$	7272$_{33}$
·434	·028 2785$_{1303}^{1306}$	5778$_{28}$	·484	·035 1771$_{1457}$	7305$_{32}$
0·435	1·028 4091$_{1308}$	0·000 5806$_{29}$	**0·485**	1·035 3228$_{1459}$	0·000 7337$_{33}$
·436	·028 5399$_{1312}$	5835$_{29}$	·486	·035 4687$_{1463}$	7370$_{33}$
·437	·028 6711$_{1315}$	5864$_{28}$	·487	·035 6150$_{1466}$	7403$_{33}$
·438	·028 8026$_{1318}$	5892$_{29}$	·488	·035 7616$_{1469}$	7436$_{33}$
·439	·028 9344$_{1318}^{1321}$	5921$_{29}$	·489	·035 9085$_{1469}^{1471}$	7469$_{33}$
0·440	1·029 0665$_{1324}$	0·000 5950$_{29}$	**0·490**	1·036 0556$_{1475}$	0·000 7502$_{34}$
·441	·029 1989$_{1327}$	5979$_{29}$	·491	·036 2031$_{1478}$	7536$_{33}$
·442	·029 3316$_{1330}$	6008$_{29}$	·492	·036 3509$_{1481}$	7569$_{33}$
·443	·029 4646$_{1333}$	6037$_{29}$	·493	·036 4990$_{1484}$	7602$_{34}$
·444	·029 5979$_{1333}^{1336}$	6066$_{30}^{29}$	·494	·036 6474$_{1484}^{1487}$	7636$_{34}$
0·445	1·029 7315$_{1339}$	0·000 6096$_{29}$	**0·495**	1·036 7961$_{1489}$	0·000 7670$_{33}$
·446	·029 8654$_{1342}$	6125$_{30}$	·496	·036 9450$_{1493}$	7703$_{34}$
·447	·029 9996$_{1345}$	6155$_{29}$	·497	·037 0943$_{1496}$	7737$_{34}$
·448	·030 1341$_{1348}$	6184$_{30}$	·498	·037 2439$_{1499}$	7771$_{34}$
·449	·030 2689$_{1348}^{1351}$	6214$_{30}^{30}$	·499	·037 3938$_{1499}^{1502}$	7805$_{34}$
0·450	1·030 4040	0·000 6244	**0·500**	1·037 5440	0·000 7839

TABLE 3.

$\alpha^{\frac{1}{2}}\sigma$	J	K	$\alpha^{\frac{1}{2}}\sigma$	J	K
0·500	1·037 5440_{1505}	0·000 7839_{34}	**0·550**	1·045 4393_{1656}	0·000 9659_{39}
·501	·037 6945_{1508}	7873_{34}	·551	·045 6049_{1659}	9698_{39}
·502	·037 8453_{1511}	7907_{34}	·552	·045 7708_{1662}	9737_{39}
·503	·037 9964_{1514}	7942_{35}	·553	·045 9370_{1666}	9776_{39}
·504	·038 1478_{1518}	7976_{34}	·554	·046 1036_{1668}	9815_{39}
0·505	1·038 2996_{1520}	0·000 8011_{34}	**0·555**	1·046 2704_{1671}	0·000 9854_{40}
·506	·038 4516_{1523}	8045_{35}	·556	·046 4375_{1674}	9894_{40}
·507	·038 6039_{1526}	8080_{35}	·557	·046 6049_{1678}	9933_{39}
·508	·038 7565_{1529}	8115_{35}	·558	·046 7727_{1680}	0·000 9972_{39}
·509	·038 9094_{1532}	8150_{35}	·559	·046 9407_{1683}	0·001 0012_{40}
0·510	1·039 0626_{1536}	0·000 8185_{35}	**0·560**	1·047 1090_{1687}	0·001 0052_{40}
·511	·039 2162_{1538}	8220_{35}	·561	·047 2777_{1689}	0092_{40}
·512	·039 3700_{1541}	8255_{35}	·562	·047 4466_{1693}	0131_{39}
·513	·039 5241_{1544}	8290_{35}	·563	·047 6159_{1695}	0171_{40}
·514	·039 6785_{1548}	8325_{36}	·564	·047 7854_{1699}	0211_{41}
0·515	1·039 8333_{1550}	0·000 8361_{35}	**0·565**	1·047 9553_{1701}	0·001 0252_{40}
·516	·039 9883_{1553}	8396_{36}	·566	·048 1254_{1705}	0292_{40}
·517	·040 1436_{1557}	8432_{36}	·567	·048 2959_{1707}	0332_{40}
·518	·040 2993_{1559}	8468_{35}	·568	·048 4666_{1711}	0373_{41}
·519	·040 4552_{1563}	8503_{36}	·569	·048 6377_{1714}	0413_{40}
0·520	1·040 6115_{1565}	0·000 8539_{36}	**0·570**	1·048 8091_{1716}	0·001 0454_{41}
·521	·040 7680_{1568}	8575_{36}	·571	·048 9807_{1720}	0495_{41}
·522	·040 9248_{1572}	8611_{36}	·572	·049 1527_{1723}	0536_{41}
·523	·041 0820_{1574}	8647_{37}	·573	·049 3250_{1725}	0577_{41}
·524	·041 2394_{1578}	8684_{36}	·574	·049 4975_{1729}	0618_{41}
0·525	1·041 3972_{1581}	0·000 8720_{36}	**0·575**	1·049 6704_{1732}	0·001 0659_{41}
·526	·041 5553_{1583}	8756_{37}	·576	·049 8436_{1735}	0700_{41}
·527	·041 7136_{1587}	8793_{37}	·577	·050 0171_{1738}	0741_{42}
·528	·041 8723_{1589}	8830_{36}	·578	·050 1909_{1741}	0783_{41}
·529	·042 0312_{1593}	8866_{37}	·579	·050 3650_{1744}	0824_{42}
0·530	1·042 1905_{1596}	0·000 8903_{37}	**0·580**	1·050 5394_{1746}	0·001 0866_{42}
·531	·042 3501_{1598}	8940_{37}	·581	·050 7140_{1750}	0908_{42}
·532	·042 5099_{1602}	8977_{37}	·582	·050 8890_{1753}	0950_{42}
·533	·042 6701_{1605}	9014_{37}	·583	·051 0643_{1756}	0992_{42}
·534	·042 8306_{1608}	9051_{38}	·584	·051 2399_{1759}	1034_{42}
0·535	1·042 9914_{1610}	0·000 9089_{37}	**0·585**	1·051 4158_{1763}	0·001 1076_{42}
·536	·043 1524_{1614}	9126_{38}	·586	·051 5921_{1765}	1118_{43}
·537	·043 3138_{1617}	9164_{37}	·587	·051 7686_{1768}	1161_{42}
·538	·043 4755_{1620}	9201_{38}	·588	·051 9454_{1771}	1203_{43}
·539	·043 6375_{1623}	9239_{37}	·589	·052 1225_{1774}	1246_{42}
0·540	1·043 7998_{1626}	0·000 9276_{38}	**0·590**	1·052 2999_{1777}	0·001 1288_{43}
·541	·043 9624_{1629}	9314_{38}	·591	·052 4776_{1781}	1331_{43}
·542	·044 1253_{1631}	9352_{38}	·592	·052 6557_{1783}	1374_{43}
·543	·044 2884_{1635}	9390_{38}	·593	·052 8340_{1786}	1417_{43}
·544	·044 4519_{1638}	9428_{39}	·594	·053 0126_{1790}	1460_{43}
0·545	1·044 6157_{1641}	0·000 9467_{38}	**0·595**	1·053 1916_{1792}	0·001 1503_{44}
·546	·044 7798_{1645}	9505_{38}	·596	·053 3708_{1795}	1547_{44}
·547	·044 9443_{1647}	9543_{39}	·597	·053 5503_{1799}	1590_{43}
·548	·045 1090_{1650}	9582_{39}	·598	·053 7302_{1801}	1633_{43}
·549	·045 2740_{1653}	9621_{38}	·599	·053 9103_{1805}	1677_{44}
0·550	1·045 4393	0·000 9659	**0·600**	1·054 0908	0·001 1721

AN OCCURRENCE OF BOUDINAGE STRUCTURE IN NEW SOUTH WALES.

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With three text-figures.

INTRODUCTION.

During an investigation of the geology of the Wantabadgery district, New South Wales, certain masses of quartzitic material roughly elliptical in section were observed interbedded with more argillaceous low-grade metamorphic rocks in the vicinity of Mundarlo (for locality see Fig. 1, inset). The arrangement resembles the structure called *boudinage* by Lohest (1909). Boudinage structures have not often been reported by geologists, in Australia at any rate, and it was therefore thought desirable to place the present occurrence on record. The aim of this note is to record the new locality and to give a brief description of the structure. Oriented specimens have been collected for the purpose of a petro-fabric examination, but this has not yet been commenced.

GENERAL GEOLOGICAL RELATIONS.

The country rocks for the most part consist of rather thick interbedded sandy and argillaceous beds believed to be of Upper Ordovician age, though reliable palæontological evidence is lacking within the area examined. Sedimentary types, corresponding to the pelites, psammopelites and psammites, recognised by Joplin at Cooma (Joplin, 1942) and Albury, are present, but the psammopelites are quite the most abundant. These sediments are now represented by phyllites, mica-schists, quartzites and quartz-rich granulites of epi-metamorphic type. The *terrain* has been invaded by a mass of partly gneissic biotite-granite, lithologically similar to the Cooma gneiss (Joplin, 1942), which is considered to be of epi-Ordovician age. Within the contact areole of this granite the argillaceous schists have developed conspicuous knots of porphyro-blastic andalusite and cordierite.

At the present time the structure of the area is far from being clear. Field-relations suggest that the bedded rocks have been tightly, almost isoclinally, folded on axes generally parallel to the north-west–south-east strike of the country. Dips are constantly steep, often nearly vertical, and the cleavage developed in the argillaceous phyllites and schists is usually parallel to the bedding.

THE BOUDINAGE STRUCTURES.

The boudins have been found in a restricted area along the dry creek in Pors. 97, 98, 169, Parish of Mundarlo, Co. Wynyard. Most of them occur in the banks of the creek, where it locally cuts across the strike of the country. All the observed outcrops are within the zone of knotted schists (Fig. 1). The structures appear only where there is a rapid alternation of psammitic and more argillaceous beds and in the vicinity of the best-developed boudins the average thickness of individual horizons is only about 2–3 inches. A few boudin-like

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blocks up to 8 inches thick have been observed in the same locality, but the field-relations are not clear.   This close bedding is in contrast with the greater part of the sedimentary series in this region, where much thicker beds are the
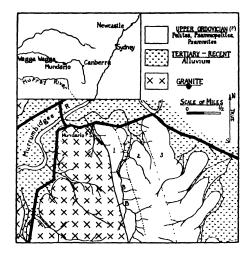
Fig. 1.—Geological sketch-map of the Mundarlo District.
Metamorphic zones shown thus :   Zone of Knotted Schists (1) ;
Biotite Zone (2) ; Chlorite-sericite Zone (3).   Boudinage occurrences
indicated by (B).

general rule.   The material of which the boudins are composed is typically a rather compact, fine-grained, slightly mottled cream to grey psammite.   In thin section it is seen to consist essentially of quartz and clinozoisite-epidote with a
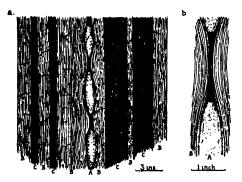
Fig. 2.

(a) Typical arrangement of boudinage at Mundarlo. From a
    photograph.
(b) The neck between two small boudins showing parallel cracks.
Psammite (A), Psammopelite (B), Knotted Schist (pelite) (C).   The
black marks at the nodes of the boudins represent quartz veins.

general granulitic appearance.   The original sediment was probably a calcareous or marly sandstone, a relatively rare type in this region.   It is interesting to note that ellipsoids of epidosite have been recorded at Broken Hill (Browne, 1922).   Their origin and significance are, however, not clear.

The Mundarlo boudins are strung out along the bedding and are only found between more argillaceous bands.   Figure 2a illustrates the best-exposed section. The major axes are parallel to the bedding and are usually about twice or three times as great as the minor axes, the average dimensions being about 4 inches and 1·5 to 2 inches respectively.   Each boudin is joined laterally to its fellow by a narrow neck composed of the same material as the main body.   Fractures have developed within the necks, and towards the shoulders some of these cracks are parallel to the margins of the boudins.   An extreme case of this parallel cracking is to be seen in Fig. 2b.   These nodal fractures are always filled with glassy quartz which usually does not enter the neighbouring beds.   These adjacent beds have a definite cleavage curved parallel to the margins of the boudins.   The effect is most marked at the nodal positions.   The undulations along the bedding caused by the alternate thickening and thinning of the psammite band are evened out in the immediately contiguous horizons (above and below).   Rarely does the disturbance proceed appreciably beyond these two beds.
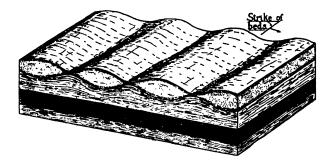
Fig. 3.—Diagrammatic representation of the probable nature of the
Mundarlo boudinage.

The third-dimensional aspect of these structures is not altogether satisfactory because the bedding-planes are not uncovered where the boudins outcrop. However, several specimens of boudins have been removed with a geological pick and they appear to be end-sections of elongated masses somewhat similar to the barrels or " sausages " of the classic boudinage of Lohest, but they are very much more flattened than the type-specimens.   Figure 3 gives a diagrammatic view of the probable nature of the boudins.   They seem to trend almost horizontally along the bedding-planes, and are thus nearly normal to the dip direction of the beds.   The length of the boudins is unknown.   A faint striation roughly normal to the length of the boudins is a constant feature but there is not much indication of lineation parallel to the flattened barrels.   Similar lineation down the dip has been observed on the s-surfaces of specimens from the same area, which, however, show no signs of boudinage.

DISCUSSION.

The term *boudinage* was first applied to regular, nearly cylindrical bodies of sandstone lying in the bedding-planes of the Devonian strata in the Bastogne district, Belgium.   These cylinders or boudins are separated from each other by sharp fractures, transverse to the bedding, and filled by spindle-shaped quartz-veins.   The adjacent less competent beds have flowed into the depressions between the boudins, which appear as regular undulations on the bedding surfaces.   In more intensely metamorphosed *terrains,* such as Scandinavia, boudinage structures have been recorded, but often they present certain modifications of the classical examples.   The columns are commonly flattened with the

major axis of cross-section parallel to the bedding. The quartz septa between boudins are more typically irregular in shape. Wegmann (1932) gives some illustrations of such modified structures. As an extreme stage Corin (1932) refers to the " *quartzites en amandes* " from the Ardennes, which were figured by Gosselet (1888, Pl. V, No. 5). The structures described in the present note rather resemble Gosselet's examples, although they are not as extreme as the " *amandes* ".

Several different explanations have been advanced to account for the origin of boudinage. These have been outlined briefly by Read (1934), who, agreeing with Corin and Wegmann, concludes that the arrangement was caused by extension in alternating competent and incompetent beds. Cloos (1946) tacitly accepts this interpretation. In his example of boudinage from Unst Read (1934) proved that the extension of the beds was due to a compressive force acting normal to the direction of stretching. Corin (1932), in his work, attributed the effect to an oblique force, the component of which on the bedding-plane was parallel to the direction of extension. In both cases, however, the result of the extension is that the competent bands are broken by transverse fractures whilst the less competent adjacent beds flow towards the gaps caused by the bending in of the edges of the resistant blocks. Quartz is simultaneously deposited in the fractures.

In the boudinage from Mundarlo a relatively great extension is indicated. The original psammitic bands were fractured but the marginal parts of the same beds were induced to flow past the ends of the broken blocks, which at the same time moved apart. The attenuated necks thus produced are in sharp contrast with the clear-cut fractures of the Belgian boudinage. It is possible that the marked secondary flow bears some causal relation to the composition of the " boudined " beds. True quartzites are not common in the vicinity of the boudinage and so no comparative estimate can be made of the influence of the lime-bearing minerals in the boudins. The cause of the extension is not yet certain. The most plausible suggestion is that the boudins occur on the limb (or limbs) of a tight fold in which there was extension normal to the axis. If, as seems likely, the folding was related to the metamorphism of the area, the flowage of the beds may have been greatly aided by the increased pressure-temperature conditions. However, many more data are required before any reliable statement can be made.

SUMMARY.

An occurrence of boudinage structure in the Upper Ordovician of the Mundarlo district, New South Wales, is recorded. The examples are small but nevertheless indicate appreciable flowage. As far as it can be seen the boudins lie parallel to the strike of the enclosing beds. The cause of the extension which produced the structures is not certain.

REFERENCES.

Browne, W. R., 1922. Report on the Petrology of the Broken Hill Region, excluding the Great Lode and its Immediate Vicinity. *Mem. Geol. Surv. N.S.W.*, No. 8, Appendix 1.

Cloos, E., 1946. Lineation, a Critical Review and Annotated Bibliography. *Geol. Soc. Amer.*, Mem. 18.

Corin, F., 1932. À propos du boudinage en Ardenne. *Bull. Soc. Belge Géol.*, 42, 101.

Gosselet, J., 1888. L'Ardenne. *Mem. Carte géol. dét. de la France.*

Joplin, G. A., 1942. The Cooma Complex. *Proc. Linn. Soc. N.S.W.*, 67, p. 156.

Lohest, M., 1909. De l'origine des veines et des géodes des terrains primaires de Belgique. *Ann. Soc. Géol. Belgique*, 36, B, 275.

Read, H. H., 1934. On the Segregation of Quartz-chlorite-pyrite Masses in Shetland Igneous Rocks during Dislocation Metamorphism, with a Note on an Occurrence of Boudinage-structure. *Proc. Liverpool Geol. Soc.*, 16, 134.

Wegmann, C. E., 1932. Note sur le Boudinage. *Bull. Soc. Géol. France*, ser. 5, 2, 477.

ENERGY TRANSACTIONS IN HOMEOTHERMIC ANIMALS.*

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Mr. President and Members of the Royal Society of New South Wales,

I thank you for the honour of being selected by you to be the Liversidge Research Lecturer for 1950. I had never an opportunity to meet Archibald Liversidge, but I knew of his devotion to Science, and so was gratified when this opportunity made it possible for me to help carry out the desires expressed in his last testament. In this you will recall, Liversidge, with deep insight, set down the reference that " . . . the lectures shall be such as will *encourage research and stimulate the lecturer* and the public to think and acquire new knowledge by research, instead of merely giving instruction in what is already known . . . " Your lecturer has been stimulated in the course of the preparation of this discourse for you : if what it contains entices any one of you to use his special skill to render more clear the chemical reactions that are responsible for energy transfer in living organisms, the hopes of Liversidge will be met.

An exhaustive discussion of the field of knowledge that it would be desirable to cover before we might be quite ready to consider what is now known of the chemical reactions involved in the energy transactions of living processes is not for this occasion, so I trust I shall be forgiven if the treatment of the subject lacks the nicety of balance which may have been achieved had the facts we have at our disposal justified more precise generalization.† But we shall, no doubt, occasionally catch a glimpse, however faint, of the general laws of energy exchange that operate in living material, and thus be encouraged to add to the pattern of knowledge that is already taking shape.

In the somewhat dismal prospect revealed by Clausius' conclusion that our world is ever moving towards a state of maximum entropy, there is one bright spot. Photosynthesis, by those autotrophic organisms which bear chlorophyll, converts a part of solar radiation into chemical energy of high potential and so initiates a series of reactions which create order out of the monotony of the more probable state that atoms of hydrogen, oxygen, carbon, nitrogen, etc., have long since assumed in the earth's atmosphere and hydrosphere. The continual renewal of life brought about in this way is a backwater contrary to the flow towards the equilibrium implied in maximum entropy ; but this state is transient—chemical reactions of living processes are poised precariously in a medium of oxygen which, although for a while their main driving force, ultimately consumes the organism that renders them possible, to degrade its ordered substance again to Nature's more probable state. Transient and somewhat feeble this contra current, but it flows to a complexity of form in which stirs thought, the mirror in which Nature views herself. We are tempted to dwell here and ask questions. Uncertain ground this, however, and perilously near the siren call of first causes. So on this occasion let us avoid it and devote our

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* The Liversidge Research Lecture delivered November 15th, 1950.

† I hope to be forgiven also for failing to mention the names of those responsible for the great volume of experimental work drawn on during the preparation of this lecture. To acknowledge even briefly those whose contributions have given form to this subject would call for a catalogue of names that would increase many times the length of this paper.

attention to phenomena—nowise less alluring to the curious—which may be interpreted through experimental enquiry.

I propose to recall for you some of the phenomena associated with the overall energy transactions that take place under conditions of relatively constant temperature in the tissues of homeothermic animals ; to seek with you to learn something of the efficiency with which these proceed ; and then to view our findings in the light of what is now known of the chemical reactions of intermediary metabolism that give rise to the free energy utilized in the process of living.
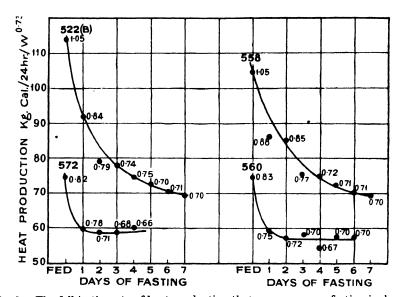
Fig. 1.—The fall in the rate of heat production that supervenes on fasting is shown by the performance of four sheep, of which two, Nos. 522B and 558, were fasted after three months on a very high level of feeding, and two, Nos. 572 and 560, after a similar period on rations which provided sufficient energy to meet only 50 per cent. of their energy requirements.

The gradual fall in the rate of energy expenditure of Nos. 522B and 558 towards the asymptote of the basal level is typical of well fed ruminants ; the slow recession being due to the buffer effect of the voluminous rumen contents, which continues to ferment and so to provide assimilable nutriment to the animal for several days after the beginning of fasting. As carnivores and mixed-feeders rapidly digest and assimilate their food, the enhanced rate of heat production brought about by the heat increment of the absorbed nutriments subsides within 12–18 hours after feeding, and so the recession to the basal level is precipitate. Subsequent to reaching the basal level, the rate of heat production of the resting animal remains unaltered for a considerable period.

Sheep Nos. 572 and 560 were already in a state of malnutrition when the observations were commenced. As they were fasted from a low level of food intake, the residual food in the rumen was small, and fermentation was complete in 48 hours, and so the rate of heat production in these fell more rapidly to the low " basal " level, which is a consequence of inanition.

The respiratory quotient of each animal during the 24 hours over which its heat output was estimated is reported at each point on the graphs.

It is not my intention to pause long in the dawn of the modern era of nutritional physiology, but our thesis will be better founded if we recall Antoine Lavoisier's last great contribution to science—his discovery of a relationship between the work performed by an animal and the oxygen it consumes—for this was indeed the sunrise. Perusal of the memoir in which Lavoisier describes the experiments that led to these conclusions still quickens the pulse, for he so

clearly delights in setting down his ideas. Here, in a manner quite foreign to his earlier writings, he exults in his argument, then, to savour it, pauses a while to philosophize, akin in style to that incorrigible moralizer Joseph Priestly ; soon to take up the threads again to discuss the effects of the ingestion of food on oxygen consumption—which incidentally will be our main concern—finally to end with an excursion into politics, pleading men to caution in the threatening storm of revolution, as if in anticipation of his own fate. This, the last and greatest of his memoirs to the Academy, contains his confession of faith ; in it he sets down two essential conditions for the advancement of knowledge— freedom of thought and the quietness of the laboratory. In the light of his experiments he had beheld the vista and declared· " *La vie est une fonction chimique* ".

Before we consider the classical theories of energy metabolism, and attempt to set them more securely in the framework of existing biochemical knowledge, we should recall the main phenomena associated with heat production in homeo- thermic animals. At this stage our concern is neither with the energy expended in voluntary muscular movement nor with the processes that are influenced through nervous and hormonal mechanisms when, in a cold environment, radiation exceeds the amount of heat liberated in the normal course of the animal's metabolism. We seek at this juncture to learn something of the rate of energy expenditure necessary merely to sustain life in the homeothermic animal, and so are at pains to eliminate as many variables as possible.

When the increased heat production that supervenes on consumption of food has subsided, a warm-blooded animal, at rest in a neutral thermal environ- ment, produces heat at a rate which for some days is tolerably uniform. During prolonged fasting—while the organism is virtually living at the expense of its own tissues—this basal rate of heat production recedes very gradually with the onset of inanition, to increase abruptly, as a symptom of the cataclysmic disorganization of the metabolic processes, immediately prior to death.

Some of the earliest observations, made over 100 years ago, showed clearly that this overall cost of living is not a direct mathematical function of the animal's size but is nearly proportional to its body surface. Literal acceptance of the Surface Law which was formulated from this observed relationship has been responsible for no little confusion. The search for a parameter to facilitate comparison of the metabolic behaviour of animals of different sizes was influenced by the implication that radiation from the body surface determines the basal rate of heat production. In consequence, elaborate measurements were made of the areas of body surfaces in order to relate them to body weights so that— questionable logic this—energy metabolism might be related to surface areas computed from body weights. All this in search of a chimera, for any generaliza- tion based on the assumption that equal areas result in equal heat losses is precluded by the widely different capacities of different parts of the body surface to radiate heat. The Surface Law, in so far as it suggests a causal relationship between the physical surface of an animal and its basal rate of heat production, is untenable.

There is, however, no question that basal metabolism varies exponentially with body weight. In homeothermic animals a relationship of this sort is clearly essential. A few simple calculations of heat exchange will suffice to indicate the necessity for the relatively great differences between the rates at which heat is produced in small and large animals. A mouse, for instance, with a basal rate of heat production per unit weight identical with that of an elephant could not live as a warm blooded animal in a temperate climate unless—strange fancy this—it were clothed in an envelope some 30 cm. thick of material with the same specific insulation as fur ; or conversely, an elephant with a metabolic

rate per unit weight identical with that of a mouse could not exist in its native habitat without a radiator of monstrous proportions. These are extremes in the phylogenetic scale, but within small limits of deviation the same exponential relationship holds for all homeothermic animals, of identical species and of different species, whatever their size.

Some such relationship could not have been other than a prime criterion which, in the course of Evolution, determined survival of the species. The precision with which Natural Selection has poised the rate of metabolism and has graded so nicely the subsidiary anatomical apparatus to fulfil its requirements of fuel and oxygen is a subject for wonder. All seems so perfectly ordered, as if one agency determines both the size and the metabolic rate of the animal ;
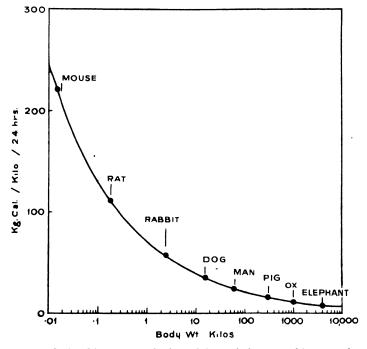
Fig. 2.—The relationship between body weight and the rate of heat production of homeothermic animals under basal conditions is plotted. The points are mean values of critical determinations. The logarithmic scale employed for the ordinate of body weights tends to obscure small deviations from the smooth curve, but there is no doubt of the overall exponential relationship.

for in such close harmony we are led to seek a single variable. Our thoughts at once fly to hormonal balance within the organism, and particularly to thyroxine with its known profound effects on both heat production and metabolism of protein, and incidentally on growth and development. But to follow such thoughts at this stage would lead us to digress. We shall return to them later.

We may accept, then, that the energy costs involved in living under basal conditions vary exponentially with the weight of the animal. Observation of the metabolism of animals varying in size from that of a mouse to that of the elephant suggest that the rate of heat production by mature animals under basal conditions will not deviate far from $70 \ W^{0.7}$ Kg. Cal. per 24 hours, where W (Kg.) is the body weight of the fasting animal. As this is an empiric expression determined from well observed experimental data, it implies no causal relationships. It is subject to small intraspecific corrections for age, sex, etc., which factors are known to influence metabolic activities.

In these considerations of the overall heat production we are dealing with a summation of the rates at which heat is produced by a number of different organs which, having in the course of ontogenesis assumed distinct functions, might be expected, *a priori*, to differ in their call for energy. Let us then examine the contributions made by individual organs to the overall heat production. A close estimate may be made of this from the rates of oxygen consumption and carbon dioxide formation, and these may be assessed directly from the rate of blood flow and the difference in composition of the arterial and venous supply to individual organs. The rate of heat production in the visceral organs is amazingly great. Under basal conditions, approximately 70 per cent. of the total heat production of man, for example, originates in the heart, kidneys, liver and brain, the combined weights of which constitute little over 5 per cent. of the total body weight (*vide* Table 1). The relatively rapid rate of heat production

TABLE 1.

Energy Dissipated by the Tissues of a 70 Kg. Man under " Basal " Conditions.

Tissue.	Weight of Organ and (Proportion of Body Weight).	Oxygen Consumption of Organ Litres O$_2$/24 hr. and (Proportion of Total Oxygen Consumption).	Heat Produced. Kg. Cal./24 hr./Kg. Tissue.
Whole body	70 Kg. (100 per cent.)	356 (100 per cent.)	23·5
Heart	0·33 Kg. (0·47 per cent.)	37 (10 per cent.)	520
Kidneys	0·33 Kg. (0·47 per cent.)	31 (9 per cent.)	440
Liver	1·6 Kg. (2·3 per cent.)	115 (32 per cent.)	335
Brain	1·4 Kg. (2 per cent.)	68·5 (19 per cent.)	225
	3·66 Kg. (5·24 per cent.)	251·5 (70 per cent.)	
Rest of body (by diff.)	66·3 Kg. (94·7 per cent.)	105 (30 per cent.)	7·4
Muscles	29·5 Kg. (42 per cent.)	58·5 (16 per cent.)	9·2

by the heart is not surprising—the work entailed in circulating the blood of a man of 70 Kg. body weight, for example, accounts for approximately 45 Kg. Cal./24 hr., which from the overall heat production implies a mechanical efficiency of close to 25 per cent. And the kidneys have extraneous work to do. Here again there is nothing to astonish us until we compute the free energy change entailed in the transport of salts, urea and water between the blood plasma and the urine, and find that the osmotic work necessary for the secretion of urine amounts to little more than 1 per cent. of the energy liberated as heat by the kidneys. Thus in the kidneys as well as in the liver and, curiously, in the brain, relatively intense chemical work proceeds continually, even when the animal is fasting and at rest. The chemical activity within these organs under basal conditions accounts for about 60 per cent. of the total heat produced by the animal. In comparison, the energy necessary to sustain the skeletal muscles in a living condition is small, smaller in fact than is implied in Table 1, because,

even when at rest, postural tonus involves some work. Why then this comparatively great intensity of activity in the visceral organs? What are the reactions which expend fuel at such a rate? And what controls them so precisely?

Before we seek an answer to these questions we might with profit consider briefly the phenomena associated with the increased heat production that supervenes on feeding. Up to this stage our concern has been with the *rate* of heat production under conditions selected in attempt to ensure a minimum expenditure of energy. This basal rate, however, is not by any means a simple expression of the minimum rate of free energy expenditure necessary to sustain
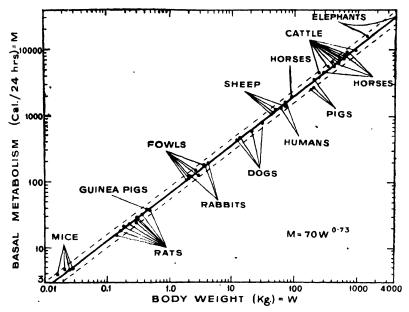
Fig. 3.—The exponential relationship between the body weight and the rated heat production of homeothermic animals under basal conditions is obvious from the above figure. The heavy line is that of the expression $M = 70W^{0.73}$ in which M is the rate of heat production in Kg. Cal./24 hr. and W is the body weight in Kg. The expression, derived empirically from observed data, is the best fit over a wide, range of animals, the body weights of which extend from 20 gm. to 4×10^6 gm. The significance of the second figure of the exponent is doubtful. The broken lines are to indicate 10 per cent. deviation from the expression.

life in the organism. Such an assumption would imply that the combustible energy of the materials drawn from the tissues of the fasting animal to support the living processes is 100 per cent. efficient for this purpose. Clearly, when considering energy transactions of this sort, we are dealing with two factors—with the demands of the organism for energy and with the efficiency with which these demands may be met by the fuel assimilated from the food or drawn from the tissues. The term " basal metabolic rate " when applied to the heat production of an animal under defined " basal " conditions is thus misleading if it is interpreted to mean the minimum rate of energy demand, and it is particularly confusing if used as a base when assessing the capacity of a foodstuff to provide the animal with the energy necessary to support its living processes—lack of appreciation of this point has resulted in a half a century of controversy.

The fact that foodstuffs differ in their ability to induce extra heat production in the animal organism was recognized early in the study of energy metabolism,

but the failure to realize that heat production is an incident, not an end, of metabolism, led, for a period, to the quite erroneous assumption that the function of a ration which would maintain a state of energy equilibrium in an animal at rest in a neutral thermal environment was merely to provide the energy necessary for the maintenance of body temperature. There is, however, ample evidence to show unequivocally that only a fraction of the combustible energy of a
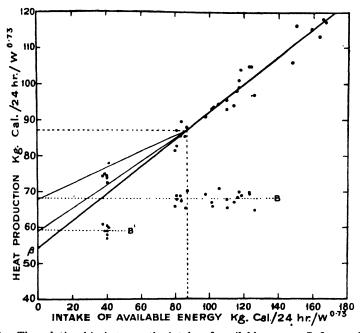
Fig. 4.—The relationship between the intake of available energy, I, from a fodder of constant composition, and the heat production, M, of sheep consuming it is plotted together with the " basal " fasting rate, B, and the inanition basal, B'. The available energy is the combustible energy of the fodder minus the sum of the combustible energy of the fodder minus the sum of the combustible energy of the fæces, urine and of the methane which is a product of fermentation in the rumen.

Above maintenance the heat produced by the animals is linearly related to the energy which becomes available from the rations. A constant proportion of the available energy—37 per cent. of it from this particular fodder—is dissipated as heat without performing any useful work in the organism. This fraction is defined as " the heat increment ". Extrapolation of the relationship to zero intake provides the term, β, which may be tentatively defined as " true basal heat production ". This is 20 per cent. less than B, the rate of heat production of the resting animal under " basal " conditions, and implies that the energy provided by fuel drawn from the tissues is subject to a heat increment of 20 per cent. Thus, below maintenance, the slope of the relationship between the heat production and the energy available from the ration, alters. In this range, it is made up of two factors, the heat increment of the fodder and the heat increment of the tissue substances drawn upon to make up the energy deficit.

maintenance ration contributes to the quota necessary to sustain life, and that the remainder merely adds to the heat production already sufficient to support body temperature.

The heat increment—that quota of the total energy available from a substance being metabolized which is dissipated as heat apparently without serving any useful purpose in metabolism—has been considered to vary with the level of feeding, for in the relationship between food intake and heat output, there is an apparent difference above and below the maintenance level. Below

maintenance, however, when the available energy of the fodder is insufficient to provide for the energy requirements of the animal, the heat increment should be considered to be made up of two variables—the heat increment of the fodder and the heat increment of the tissue substance being drawn upon to make up the net energy deficit—and so, if these differ, the capacity of the fodder to provide useful energy would appear to alter abruptly as soon as energy equilibrium is established.

To illustrate these points let us consider, very briefly, the relationship between heat production and the intake of available energy, of sheep fed different quantities of the same foodstuff. It might be well to recall that the determination of the heat production of the ruminant entails special problems as by far the greater proportion of the energy that becomes available to the animal from the
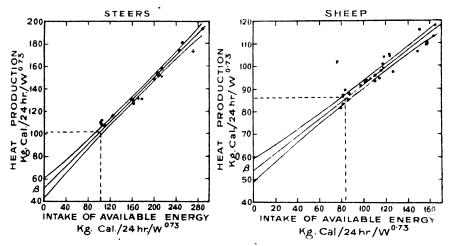
Fig. 5.—The apparent constancy of β, the point at which the linear relationship between heat production of an animal and the energy which becomes available to it from a fodder of constant composition, is illustrated by plotting two sets of independently observed data, one from observations on sheep and one from observations on cattle.

From the former, $\beta = 54 \cdot 5$ Kg. Cal./$W^{0 \cdot 73}$/24 hr. and from the latter $\beta = 51 \cdot 8$ Kg. Cal./$W^{0 \cdot 73}$/24 hr., the difference being well within the standard error of the observations.

β is tentatively defined as " true basal rate of heat production " for the convenience of assessing the relative heat increments of the available energy from various fodders. The term " basal " does not imply that β is a measure of the minimum expenditure of energy necessary to support the living processes, but, in distinction to its more general use to define the exogenous conditions under which heat production is estimated, it connotes in this expression an endogenous constant common to the metabolism of all foodstuffs.

carbohydrates in its fodder is derived from simple fatty acids produced by fermentation in the paunch. The chemical changes involved in the formation of these fatty acids through the activity of micro-flora are exothermic. The amount of heat dissipated during fermentation is approximately 6 per cent. of the combustible energy of the carbohydrates transformed. This quota of energy, like that of the heat increment, is valueless in the economy of the animal, other than when, in a cold environment, the amount of heat lost by radiation from the body surface is greater than that produced in the normal course of metabolism—under which circumstances, as a part of the overall heat increment, it spares, calorie for calorie, the energy that would be called upon merely to provide heat for the maintenance of body temperature. The heat production of the fed

ruminant is thus the sum of the heat produced as an end result of metabolic processes of the animal itself and the heat evolved by the fermentative activity of the microorganisms of its alimentary canal.

When the whole of the animal's energy requirement is drawn from the fodder, there is no reasonable doubt that *the relationship between intake of available energy and heat production is linear*. The heat increment quota is *thus a constant proportion of the available energy*—in this particular instance 37 per cent. of the available energy is dissipated as heat in the chemical work necessary to prepare the absorbed nutrients for their entry into the chain of events through which, according to the supply and demand, they may either be launched into the energy-producing cycles or laid down as body substance (Fig. 4).

Extrapolation of this linear relationship to the heat production axis should allow a close estimate to be made of the overall amount of energy spent on the physiological requirements of living, uninfluenced by the heat increment of the materials oxidized to provide this energy. Thus the intercept, β, which we might call tentatively the " true basal requirement ", is less than B, the actual heat production under basal conditions (Fig. 4), by the heat increment of the fuel drawn from the body substance—which from this estimate is close to 20 per cent. of the total heat dissipated during fasting.

Theoretically, within the limits of the $W^{0.7}$ exponential relationship between metabolic rate and body weight, the value of β should be identical for all homeothermic animals. There is only one set of independent observations in the scientific literature that provides suitable data for testing this hypothesis— that gathered from a fine series of critically conceived and meticulously observed determinations of the heat output of bullocks fed at different planes on rations of identical composition (Fig. 5). The intercept, β, at which the extrapolated regression of the heat production : available energy relationship cuts the heat production axis in this case indicates a value 51·85 Kg. Cal./$W^{0.7}$/24 hr. with a standard deviation of 3·38 ; the value of β derived similarly from experiments with the sheep is 54·56 Kg. Cal./$W^{0.7}$/24 hr. with a standard deviation of 2·30. What then is implied in this apparently constant figure ? We may be better prepared in our attempt to answer this question if we recall something of what is known of the transformations involving energy exchange that take place in the course of intermediary metabolism.

We can be sure that free energy is not liberated in one burst when substrates are oxidized within the cell. The abrupt gradient in the passage of electrons towards oxygen that such an event would imply is lessened by an ordered series of reactions, guided through the maze of thermodynamic possibilities by inter-linked specific catalysts that convey, by transphosphorylations, part of the free energy to compounds of relatively low molecular weight. From our present state of knowledge it appears not improbable that adenosine triphosphate assumes in this way the main role of carrier of energy within the cell, weaving between the sites where free energy is rendered available by respiration, and the sites where chemical work is to be done, bearing in the resonance of its pyro-phosphate group a versatile means of energy exchange for the performance of work within the cell—one is tempted to consider this resonance energy to be universal currency in living matter.

During respiration within the cell, three steps are now known to be capable of intervening between the liberation of two hydrogen atoms from the substrate and their final combination with oxygen—the stages marked successively by reactions with the co-enzyme pyridine-nucleosides, which occur at E'_0 potentials about -0.32 v. ; the reactions with the flavo-proteins, the protein complexes of d-ribityl 6 : 7 dimethyl-iso-alloxazine nucleoside, which occur about -0.6 v. ; and the reactions with the iron-bearing cytochromes, which occur about $+0.39$ v.

A path such as this, in which each pair of electrons is intercepted three times at intervals during their journey between the substrate and oxygen, would impose a thermodynamic limit to the number of coupled reactions which could be brought about.   Thus, if this path were traversed, the transphosphorylating
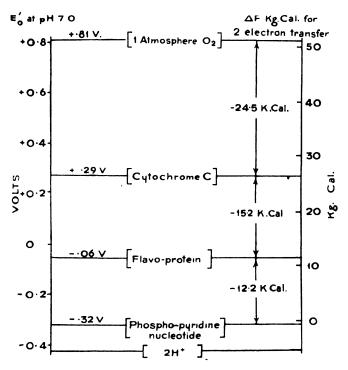
Fig. 6.—The free energy changes which would take place, when, during respiration within the cell, two electrons, set free by a dehydrogenating reaction, pass from the substrate, via phospho-pyridine nucleotide, flavo-protein and the cytochromes, to oxygen, may be assessed from the above figure.

The scale of oxidation-reduction potential E'_0 at pH $7 \cdot 0$, which is a measure of the free energy of the reactions involved, expresses, in volts, the difference of potential between the system at pH $7 \cdot 0$ and the normal hydrogen electrode (pH $= 0$). The signs and the zero of this conventional scale are thus consequences of the mathematical convenience in the selection of the normal hydrogen electrode potential as a reference point.   The chemical potential, i.e. the relative tendency for electron flow, of these reactions decreases progressively as the potential of oxygen is approached.

The scale of free energy changes is derived from the relationship, $-\triangle f = nF \triangle E$, in which $\triangle f =$ the change in free energy in Joules, $n =$ the number of electrons involved, $F =$ the Faraday, and $\triangle E =$ the potential difference in volts.

As the average resonance energy in pyrophosphate bonds, $\sim P$, is close to 12 Kg. Cal./mole, which is equivalent to approximately $0 \cdot 25$ volt per two electron transfer, four coupled reactions, each involving the production of one $\sim P$, are the thermodynamic limit if the above course is taken, one in the $0 \cdot 26$v. interval between phospho-pyridine nucleotide and flavo-protein, one in the $0 \cdot 33$v. interval between flavo-protein and the cytochromes, and a possible two in the $0 \cdot 52$v. interval between the cytochromes and oxygen.

reactions which convert adenosine diphosphate to adenosine triphosphate and thereby convey 12 Kg. Cal./mole in the resonance of the added pyrophosphate group, would be limited to four, for each atom of oxygen consumed.   Available evidence suggests that only three such transfers are achieved.   This would imply the dissipation as heat of 30 per cent. of the free energy liberated by each

dehydrogenation—the remaining 70 per cent. being converted to resonance energy capable of performing work within the cell.

Some of you may recall that classical physiologists considered glucose " the preferred fuel " for the provision of energy to the organism. Let us, then, examine what is known of free energy changes which occur during oxidation of a glucose molecule within the cell. Glycolysis, you will agree, is now reasonably well understood to be a series of reversible reactions—extending in the animal organism between glycogen and pyruvic acid—through which glucose passes
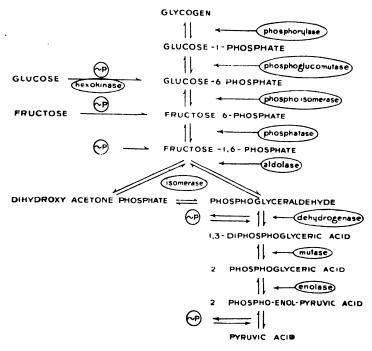
Fig. 7.—The probable course taken by glucose during glycolysis within animal tissues is indicated. The reactions between the links are reversible, the equilibria being influenced primarily by the concentration of adenosine triphosphate, the resonance energy of the pyrophosphate group of which is indicated by ∼P. Conversion of glucose to glucose-6-phosphate in which form it is introduced into the glycolytic chain involves the expenditure of one ∼P. The activity of hexokinase, which effects this priming reaction, is subject to hormonal control.

before its degradation product, pyruvic acid, enters the main energy-producing cycle where oxidation is completed. Admission of glucose into this chain of events necessitates its preliminary conversion to the Robinson ester, glucose-6-phosphate, by the intervention of the enzyme, hexokinase, and of adenosine triphosphate—a synthesis which entails the expenditure of 12 Kg. Cal./mole. from a pyrophosphate group to produce an ester-phosphate in which the resonance energy is in the vicinity of 3 Kg. Cal./mole. This priming reaction is thus exothermic and irreversible. Incidentally, the enzyme that affects it is now known to be subject to hormonal control—hexokinase activity is apparently poised between the inhibitory influences of anterior pituitary and adreno-cortical hormones and the stimulatory influences of insulin.

Once glucose is introduced into the glycolytic chain as glucose-6-phosphate its conversion through the Cori ester, glucose-1-phosphate, to glycogen, or its

degradation via fructose-6-phosphate to the Harden-Young ester, fructose-1, 6 phosphate—by means of phosphatase and the intervention again of adenosine triphosphate, at this stage to convey a recoverable unit of 12 Kg. Cal./mole—hence via the triose, phosphoglyceraldehyde, by dehydrogenation to 1,3-diphosphoglyceric acid, and then in turn through 2,phosphoglyceric acid and phosphoenol-pyruvic acid to pyruvic acid, is apparently a matter of equilibria, influenced by the relative concentrations of the reacting links, and of the availability of adenosine triphosphate. The resonance energy of two pyro-phosphate groups of adenosine triphosphate are expended in this series of changes and four are recovered. Thus, during the degradation of a glucose unit from glycogen through these reactions to two molecules of pyruvic acid, recovery in terms of the energy transferred to pyrophosphate groups—i.e. in currency expendable on work within the cell—is approximately 35 per cent. of the energy set free. The overall recovery of energy from the glycolytic reactions if glucose itself is the starting point is further reduced to approximately 20 per cent. by the cost of the priming phosphorylation.* But the major part of the potential energy of the glucose molecule (83 per cent. of it) is retained in the two molecules of pyruvic acid. The overall cost, then, in preparing glucose for its excursion into the tricarboxylic acid cycle is about 14 per cent. of its combustible energy. While considering these reactions in some detail I have perhaps tried your patience, but in recalling them, my purpose is to stress that there are considerable expenses in terms of energy which must be met before even " the preferred fuel " is converted to a form in which it may be launched into the cycle which apparently is the main convertor of energy in the living cell.

The reactions of the tricarboxylic acid cycle which are now known—and which possibly are the more important ones—are no doubt familiar to you all, so I shall not try your patience further by discussing them in any detail. However, it might be well to bear in mind that the path taken by electrons liberated from some of the dehydrogenations in the respiratory cycle remains obscure. But once launched into this cycle, the 2-carbon fragment from all metabolites might be expected to yield the same amount of energy to phosphate bond resonance.

When discussing the coupled reactions that take place after electrons are liberated by dehydrogenation of the substrate, we concluded that the highest efficiency of energy transfer, which may be expected if the course suggested were taken, could not exceed 80 per cent. and that from experimental evidence available, which implies three transphosphorylations for each atom of oxygen consumed in the tricarboxylic acid cycle, the efficiency would probably be closer to 70 per cent. If this estimate is correct, oxidation of the two moles of pyruvic acid would transfer to adenosine diphosphate approximately 360 Kg. Cal. as resonance energy in pyrophosphate groups. Complete oxidation of a molecule of glucose, then, would yield in this currency close to 55 per cent. of the total free energy liberated—there is a net gain of 24 Kg. Cal./mole, it will be recalled, in the glycolytic reactions through which the glucose molecule is degraded to two molecules of pyruvic acid.† Thus it becomes evident that the net recovery of energy in a state capable of performing work within living tissues, falls far short of the total energy liberated during complete oxidation of a substrate.

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* Conversion of one mole of glucose to two moles of pyruvic acid involves a free energy change of −115 Kg. Cal. As the resonance energy, $\sim$P, of the pyrophosphate group of adenosine triphosphate is approximately 12 Kg. Cal., the net recovery of energy in this currency is about 24 Kg. Cal.—the total recovery being 4$\sim$P and the expenditure 2$\sim$P. The efficiency of the reaction in terms of resonance energy is thus approximately 20 per cent.

† Recovery of energy in the resonance of $\sim$P (approx. 12 Kg. Cal./mole) on complete oxidation of a mole of glucose during respiration within the cell would be : from glycolysis, 2$\sim$P ; and from oxidation of the two moles of pyruvic acid arising from glycolysis, 30$\sim$P, i.e., 384 Kg. Cal. from a total free energy change of 674 Kg. Cal.

Although fats take a course which, as yet, is not as well charted as the one taken by carbohydrates, their relatively low heat increment suggests that the higher fatty acids are launched into the reversible channels of metabolism with an efficiency comparable with that of glucose. Acetic acid—an important

CH₃
|
C=O
|
COOH
Pyruvic acid

|-CO₂

2 CARBON INTERMEDIATE

-2H   -2H

COOH   COOH   COOH   COOH
| | | |
C=O   C-H   +H₂O H-C-OH   C=O
| +H₂O || -CO₂ | |
C COOH -CO₂ C-COOH   H-C-COOH   H-C-COOH
|| | | |
C-H   H-C-H   H C H   H-C-H
| | | |
COOH   COOH   COOH   COOH

oxalo-citraconic acid   cis-aconitic acid   iso-citric acid   oxalo succinic acid

? ~P   ? ~P

-2H ← ~~~ 3 ~P   -CO₂.

1 ~P   1 ~P   3 ~P

                                                    COOH
                                                    |
                                                    C=O
COOH   COOH   COOH   COOH |
| | | | H-C-H
C=O   ~   H-C-OH +H₂O C H   ~   H-C-H   +H₂O |
| | || | -CO₂   H-C-H
H-C-H   H-C-H   C H   H C H |
| | | | COOH
COOH   COOH   COOH   COOH

oxal acetic acid   malic acid   fumaric acid   succinic acid   α-keto glutaric

-2H   -2H

Fig. 8.—The known reactions of the tricarboxylic acid cycle through which respiratory dehydrogenation of many substrates is effected, are set out. Knowledge of these reactions has been achieved, for most part, from studies, *in vitro*, with tissue extracts and suspensions. The yield of ~P from the transphosphorylating reactions coupled to each stage of dehydrogenation is not yet clear. Experimental determination of the overall relationship between the amount of oxygen consumed and the yield of ~P during cellular respiration suggests that the production of 3~P is achieved at each stage. The thermodynamic limit would be 4~P. (*vide* Fig. 6.)

fuel for ruminants—is apparently a much more expensive unit to launch into these channels, and for this reason is probably responsible for a major part of the relatively high rate of heat production in the fed ruminant. Propionic acid, which is formed along with acetic acid during fermentation of carbohydrates in the rumen, certainly has a materially smaller heat increment than that of acetic acid.

The heat increment of the available energy from protein is notoriously high. Here, however, we might expect the costs entailed in the formation and excretion of urea to be superimposed on the heat increments of the various fragments that arise from the deaminized amino acids, some of which take the metabolic course of the carbohydrates, some the course of the higher fatty acids, and some, like acetic acid, a much more expensive course. The costs of the chemical work necessary for the production of urea in the ornithine cycle, and for the osmotic work necessary for its excretion, must be discharged with the depreciated currency of resonance energy, and so are greater than those implied from the overall free energy change.

Hitherto I have refrained from employing the classical term " specific dynamic effect ", which has been considered to be synonymous with " heat increment ". I have avoided it because it implies that the increase of heat production which supervenes on the consumption of food is the result of a stimulus to metabolism—of an increase in the demands for energy by the tissues rather than a consequence of the costs entailed in the launching of the foodstuffs into channels through which these demands may be fulfilled. But the term and its implications may not lightly be dismissed when considering the effect that protein ingestion exerts on the heat production of animals, for it is conceivable that the dynamic equilibrium, which exists between the metabolic pool of amino acids and the tissue proteins, may be influenced by the amino acids arising from the ingested protein to an extent that might increase materially the expenditure of energy necessary to sustain protoplasmic structure.

Let us consider, very briefly, the energy transactions involved in this equilibrium, as they will serve, *inter alia*, to illustrate the relatively great losses of energy entailed in the performance of the chemical work in living tissues.

We have discussed the evidence which renders it probable that resonance energy of pyro-phosphate groups constitutes a most important currency for the performance of work in living tissues. The exchange rates for conversion of the energy liberated by respiration to this currency are obviously high, and—to continue the metaphor—its purchasing power in terms of chemical work is, more often than not, very low. For instance, the costs of synthesizing a peptid bond between two amino acids, which effects a free energy increase of about 3 Kg. Cal./mole, involves the expenditure of the whole of the resonance energy of the pyro-phosphate group of adenosine triphosphate, with the dissipation of 75 per cent. of it. Thus, synthesis of protein is a costly item in the economy of the organism ; its efficiency in terms of the " preferred fuel " would not exceed 14 per cent., and, in terms of the fuel absorbed from the intestinal tract of ruminants, would be reduced further by the heavy losses involved in the high heat increment. A considerable amount of energy is clearly necessary to maintain the structure of protoplasm, for there is no doubt that the proteins in living cells are in constant flux and that their apparent steady state is but a reflexion of the relative rates of their degradation and resynthesis. From experiments in which N^{15}-tagged amino acids were fed to humans and to rats there is eloquent evidence to indicate that the rate of protein turnover within the tissues of a homeothermic animal in a steady nutritional state, varies with the size of the animal. The ratio of the rates of protein synthesis per unit weight of the rat and of Man, estimated by this means, is very close to 5 : 1—practically identical with the relative rates of energy expenditure under basal conditions. We have already concluded (Table 1) that the heat production within the liver accounts for over 30 per cent. of the total heat production of Man under basal conditions. The rate of protein turnover in the liver of Man, assessed from the rate of loss of N^{15} from the blood-plasma proteins, which there is good reason to believe are produced in the liver and are in dynamic equilibrium with the liver

protoplasmic proteins, bears a similar relationship to the overall rate of protein turnover. And the comparatively slow rate of protein turnover in the muscles is closely parallel to their basal heat production.

These relationships can hardly be fortuitous. They suggest that the mechanism which poises the basal rate of heat production might operate by influencing the rate of protein turnover. But, in so far as the latter may be estimated from exchange reactions, the energy cost of the syntheses necessary to preserve the tissue proteins in a steady state is not of the same order as the energy dissipation implied by the total heat production, even when the depreciated rate of the currency which effects these syntheses is accounted for. Nevertheless a common factor is suggested and we are impelled to seek it, for knowledge of the mechanism involved would greatly clarify the central problem of energy metabolism. Although many suggestive clues are available, no satisfactory explanation of the mechanism through which the rate of heat production is poised in homeothermic animals emerges from our present state of knowledge. It is not yet clear whether the nervous and hormonal agencies primarily responsible for the overall rate of heat production in the resting animal, exert their influence by altering the demands of the tissues for energy, or by altering the capacity of the fuel to meet these demands. The former influence could operate by controlling the relative rates of the hydrolyses and syntheses which determine the dynamic state of protoplasmic constituents. The latter could operate by controlling the series of equilibria between the links of the chain of intermediary metabolic events through which the universal currency of resonance energy is produced. Direct hydrolysis of adenosine triphosphate, by phosphatase, with the dissipation of its resonance energy without performance of chemical work could, in this way, alter very materially the rate of fuel consumption.

In both of these effects enzyme systems would be involved, and there is, already, unequivocal evidence in the case of hexokinase that some at least of the known hormones exert their profound physiological effects by influencing the activity of specific enzymes.

We might speculate without end, and progress little without experimental evidence, however, and we must leave this question unanswered, along with many of the others which have confronted us during our somewhat superficial survey of energy metabolism. But, the course towards the solution of some at least of the problems which have intrigued physiologists for more than a century is now clear enough to invite the curious : and it is perhaps not too much to expect that a great clarification of our knowledge of energy transactions in living matter will soon be achieved.

In our excursion this evening, we have failed to discover any clue which might help explain the high rate of energy dissipation that occurs in the brain. We may, however, be reasonably sure that this expenditure is not directly concerned with the elaboration of that tenuous secretion, thought. We may thus take heart, for this final product of the ephemeral turbulence in the universal flow towards maximum entropy apparently calls for extremely little expenditure of energy.

Gentlemen, I thank you for your attention. If I have provoked rather than diverted you, my task is fulfilled, for I have attempted to carry out the reference set down by Archibald Liversidge and conveyed to me in your invitation.

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HALOGENOSTANNATES (IV) OF SOME COMPLEX CATIONS.

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Tin in the oxidation state of $+4$ is characterized by forming compounds with halogens of the type SnX_4 and SnX_6^-. Compounds of SnX_4 that have been examined have a tetrahedral structure and are presumably using sp^3 bonds. For salts containing the $SnCl_6^-$ ion the octahedral arrangement has been confirmed for the K, Rb, Cs, NH_4 and Tl compounds (Wells, 1945).

Octahedral bonds from an element such as tin differ from those which occur in a complex such as $PtCl_6$'. This ion has d^2sp^3 orbitals available and these after hybridization give bonds of nearly maximum strength. Octahedral d^2sp^3 bonds for Sn involves the use of d orbitals with the same principal quantum number as the s and p orbitals (Kimball, 1939). From the observed values of interatomic distances in $SnCl_6^-$ Pauling (1944) has assigned the octahedral bonds to the $5s\ 5p^3\ 5d^2$ orbitals, use being made of the unstable 5d orbitals of the valence shell itself.

The formation of the hexahalogenostannate ion takes place by reaction of the SnX_4 molecule with excess halide ions

$$SnX_4 + 2X^- \longrightarrow SnX_6{}^{2-}.$$

The reaction appears to take place more readily and the compounds formed are more stable with the increasing electronegativity of the halogen. Thus the fluoro and chloro-stannate ions are well defined and numerous compounds are known (Mellor, 1927), but the bromo and iodo-stannates are not so well characterized.

In this investigation we have prepared some chlorostannates and bromostannates of complex cobalt cations and two iodostannates of complex ferrous ions. These are listed below :

I. Tris(ethylenediamine) cobalt (III) bromide bromostannate (IV), 1-hydrate

II. Trans-dibromo-bis-(ethylenediamine) cobalt (III) chlorostannate (IV)

III. Trans-dibromo-bis-(ethylenediamine) cobalt (III) bromostannate (IV)

IV. Tris(1 : 10 phenanthroline) iron (II) iodostannate (IV)

V. Tris(22' dipyridyl) iron (II) iodostannate (IV).

They are all well defined, coloured, crystalline substances sparingly soluble, but completely hydrolysed in hot water. Analogous types of compounds to I, II and III have been previously reported : [Co en$_3$]Cl.SnCl$_6$.2H$_2$O (McCutcheon and d'Ouville, 1947) [Co en$_2$Cl$_2$]$_2$SnCl$_6$ (Spacu and Spacu, 1931), [Coen$_2$Cl$_2$]$_2$SnBr$_6$ (Spacu and Spacu, 1932). We have repeated the preparation of these compounds in order to compare them with the above. In contact with cold water, it was found that the bromo-stannates decomposed more rapidly than the corresponding chlorostannates, also decomposition was more rapid with

compounds containing the cation $[Co\ en_3]^{+++}$ than with corresponding halogenostannates containing $[Co\ en_2X_2]^+$ (En=ethylenediamine, X=Cl, Br). The iodostannates IV and V did not appear to hydrolyse to any extent in cold water, probably due to their insolubility. The only compounds containing the SnI_6^- ion so far reported are Cs_2SnI_6, Rb_2SnI_6 and $[(CH_3)_4As]_2SnI_6$, prepared by Auger and Karantassis (1925).

<div align="center">EXPERIMENTAL.</div>

I. *Tris(ethylenediamine) cobalt (III) bromide bromostannate (IV)—1-hydrate.*

[Co en$_3$]Br$_3$ was prepared by a similar method to that given for [Co en$_3$]Cl$_3$ (Fernelius, 1946). The product was dried at 120° C.

Found : Br, 50·05%.

Calculated for [Co en$_3$]Br$_3$: Br, 50·07%.

Tris(ethylenediamine) cobalt (III) carbonate, prepared from [Co en$_3$]Br$_3$ and Ag$_2$CO$_3$, was added slowly to a concentrated aqueous solution of H$_2$SnBr$_6$.8H$_2$O and the mixture warmed. Product was washed with ice cold HBr and dried at 110° C. No further loss in weight occurred after drying over P$_2$O$_5$.

Found : Sn, 12·5% ; Br, 59·6% ; N, 9·05%.

[Co en$_3$]BrSnBr$_6$.H$_2$O requires : Sn, 12·69% ; Br, 59·81% ; N, 8·99%.

The orange tetragonal crystals are immediately hydrolysed in cold water to SnO$_2$ hydrate. The compound cannot be recrystallised from HBr ; it dissolves in HBr (5 g. requires 80 ml. boiling 48% HBr) and yields [Co en$_3$]Br$_3$.3H$_2$O on cooling.

Found : Br, 45·5%.

Calculated : Br, 45·0%.

II. *Trans-dibromo-bis(ethylenediamine) cobalt (III) chlorostannate (IV).*

Trans [Co en$_2$Br$_2$]Br.HBr was prepared by treating aqueous trans [Co en$_2$Cl$_2$]Cl with Ag$_2$O, filtering and evaporating the filtrate to dryness with HBr (Mellor, 1935).

Found : Br, 63·65%.

Calculated for [Co en$_2$Br$_2$]Br.HBr : Br, 63·96%.

An aqueous solution of trans [Co en$_2$Br$_2$]Br.HBr was added to a solution of H$_2$SnCl$_6$ in concentrated HCl and warmed on a water bath. On cooling, bright green perfectly formed rhomb shaped crystals were deposited. These were washed with HCl and dried at 110° C.

Found : Sn, 11·7% ; Br, 32·8% ; Cl, 20·2% ; Co, 11·4%.

[Co en$_2$Br$_2$]$_2$SnCl$_6$ requires : Sn, 11·76% ; Br, 31·67% ; Cl, 21·08% ; Co, 11·68%.

Hydrolysis in cold water is slow ($\frac{1}{4}$-$\frac{1}{2}$ hour) ; the compound is soluble in 10% aqueous solution of H$_2$SnCl$_6$ from which it crystallizes on cooling.

III. *Trans-dibromo-bis(ethylenediamine) cobalt (III) bromostannate (IV).*

[Co en$_2$CO$_3$]$_2$CO$_3$ (reddish violet) was prepared by heating an aqueous solution of trans [Co en$_2$Cl$_2$]Cl with Ag$_2$CO$_3$—cf. Mellor, *Inorg. and Theor. Chem.*, 14, 819—filtering and concentrating the filtrate. Titration with cold standard HCl gave an equivalent weight of 268 ; one replaceable CO$_3$ group requires equivalent weight of 269·2.

[Co en$_2$CO$_3$]$_2$CO$_3$ was added to an excess of H$_2$SnBr$_6$.8H$_2$O dissolved in a minimum quantity of 48% HBr. At first the mixture remained reddish violet (cis form) (Mellor, 1935), but on heating on a water bath for ten minutes the product became yellowish green (trans form). The compound was washed with HBr and dried at 110° C.

Found : Sn, 9·2% ; Br, 62·0% ; N, 8·62% ; Co, 8·75%.

[Co en$_2$Br$_2$]$_2$SnBr$_6$ requires : Sn, 9·31% ; Br, 62·62% ; N, 8·78% ; Co, 9·24%.

P

Recrystallization from HBr (1 g. requires 60 ml. boiling HBr) is accompanied by a small amount of decomposition.

Found : Sn, 8·6% ; Br, 61·0%.

The bright yellowish green cubes and prisms decompose in cold water, yielding SnO_2 hydrate, somewhat more rapidly than the chlorostannate.

IV. *Tris(1 : 10) phenanthroline iron (II) iodostannate (IV).*

Tris(1 : 10 phenanthroline) iron (II) iodide 1-hydrate was prepared from 1 : 10 phenanthroline 1-hydrate (m.pt. 99° C.), $FeSO_4(NH_4)_2SO_4.6H_2O$, and KI in aqueous solution and recrystallized from water.

Found : N, 9·84% ; H_2O, 2·14%.

Calculated for $[Fe(C_{12}H_8N_2)_3]I_2.H_2O$: N, 9·68% ; H_2O, 2·08%.

1·0 g. $[Fe(C_{12}H_8N_2)_3]I_2.H_2O$ was dissolved in methanol and added slowly, with stirring, to a methanol solution containing 0·75 g. SnI_4 and 3 ml. 66% HI. The mixture was warmed to 50° C., stood half an hour, cooled in ice, then filtered, washed well with methanol and dried at 110° C. The product consisted of dark red prisms. Yield, 1·40 g.

Found : Sn, 8·0% ; I, 51·6% ; N, 5·77%.

$[Fe(C_{12}H_8N_2)_3]SnI_6$ requires : Sn, 8·04% ; I, 51·56% ; N, 5·69%.

Attempts to prepare this compound, using NaI in place of HI, failed. Products were obtained which gave reproducible analysis figures, in which the N : I ratio was 1 : 1 but the tin content was high.

Found : Fe, 3·35, 3·30% ; N, 5·07, 5·16% ; Sn, 8·7, 8·7% ; I, 46·5%. This gives Fe : N : Sn : I = 0·985 : 6·00 : 1·20 : 6·00.

Hence it appears that the presence of HI in the methanol solution is necessary to stabilize the $SnI_6^=$ ion ; sodium iodide is unable to prevent some of the SnI_6^- being converted to SnO_2.

V. *Tris(2,2' dipyridyl) iron (II) iodostannate.*

1 g. of tris(2,2' dipyridyl) iron (II) iodide dissolved in methanol was slowly added to a methanol solution containing 0·81 g. SnI_4 and 2–3 ml. 66% HI. After warming to 50° C. and cooling, the reddish black crystals were washed with methanol and dried at 110° C. Yield : 1·25 g.

Found : N, 6·15% ; I, 53·6%.

$[Fe(C_{10}H_8N_2)_3]SnI_6$ requires : N, 5·98 ; I, 54·20%.

As with the 1 : 10 phenanthroline compound when NaI was used in place of HI, a product was obtained in which the percentage of tin was high.

Found : N, 5·10% ; Sn, 9·5, 9·5% ; I, 49·0%, i.e. N : Sn : I = 5·50 : 1·24 : 6·00.

SUMMARY.

The chlorostannate and bromostannate of the complex cation $[Co\ en_2Br_2]^+$, the bromostannate of $[Co\ en_3]^{+++}$ and iodostannates of $[Fe(ophen)_3]^{++}$ and $[Fe(dipy)_3]^{++}$ have been prepared as well-defined coloured crystalline compounds (en = ethylenediamine ; ophen = 1 : 10 phenanthroline ; dipy = 22' dipyridyl). With the trivalent cation $[Co\ en_3]^{+++}$ only a compound containing a mixed anion—bromide + bromostannate—could be obtained. The analogous chlorostannate is similar. All the compounds are completely hydrolysed in hot water. In cold water, the bromostannates decompose more readily than the corresponding chlorostannates.

REFERENCES.

Auger and Karantassis, 1925. *Compt. Rend.* **180**, 1845.

Fernelius, W. C., 1946. Inorganic Synthesis, **2**, 221, 223. McGraw Hill, New York.

Kimball, G. E., 1939. *J. Chem. Phys.*, **8**, 188.

McCutcheon, T. P., and d'Ouville, E. L., 1947. *J.A.C.S.*, **69**, 989.

Mellor, J. W., 1927. Inorganic and Theoretical Chemistry, **7**. Longmans Green, London.

——————— 1935. Inorganic and Theoretical Chemistry, **14**.

Pauling, L., 1944. The Nature of the Chemical Bond. Cornell University Press, New York.

Spacu, G., and Spacu, P., 1931. *Bull. Soc. Stiinte Cluj*, **5**, 473.

——————————— 1932. *Bull. Soc. Stiinte Cluj*, **6**, 384.

Wells, A. F., 1945. Structural Inorganic Chemistry. Oxford Press.

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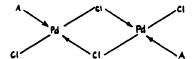
PALLADIUM COMPLEXES.

PART II. BRIDGED COMPOUNDS OF PALLADIUM WITH o-METHYL-MERCAPTOBENZOIC ACID.

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and R. A. PLOWMAN, B.Sc., A.S.T.C.

Mann and Purdie (1935, 1936) prepared bridged compounds of palladium with trialkyl phosphines and arsines of the type

where $A = (C_4H_9)_3P$ and $(C_4H_9)_3As$.

These were prepared by the action of ammonium chloropalladate (II) on the dichloro-bis(tributyl-phosphine or arsine) palladium (II) compounds. They reported difficulty with the corresponding reaction using the dialkyl sulphide compound. Mann and Wells (1938) by X-ray examination showed that the trimethyl-arsine analogue had the trans structure. They also prepared similar compounds with $-Br$, $-NO_2$, and $-SCN$ in place of $-Cl$ in the bridging positions.

As part of the systematic examination of the bridged compounds prepared by Mann *et al.*, Chatt and Mann (1939) reported that compounds in which the two arsine groups were contained in a chelate molecule did not react with ammonium chloropalladate (II) to form bridged complexes.

In the previous communication (Livingstone, Plowman and Sorenson, 1951), it was reported that o-methyl-mercaptobenzoic acid functioned as a chelate group and formed with palladium the compound bis(o-methyl-mercapto-benzoato) palladium (II), I. Potassium chloropalladate (II) solution added to the solution of I produced II from which the two molecules of water were expelled at a temperature just below decomposition. If, on the other hand, the procedure was reversed and a solution of I was added to potassium chloropalladate (II) solution the product III was anhydrous. Moreover, II consisted of deep orange tetragonal prisms of m.pt. 214° C., while the yellowish brown tetragonal prisms of III had a m.pt. of 224° C.

The empirical formulæ of these compounds are $(C_8H_7O_2S)PdCl.H_2O$ and $(C_8H_7O_2S)PdCl$ respectively. It is almost certain that these compounds are dimeric (Mann and Wells, 1938), but they are insoluble in organic solvents and the molecular weights were not determined.

Assuming that the compounds are dimeric, there appears to be no alternative formulation of III in which one chelate group is attached to each palladium atom.

This substantiates that the formation of the bridged compounds prepared by Mann and his co-workers takes place thus :

and not

There remains to consider the relationship between II and III. The possibilities appear to be limited to

(i) dimorphous forms ;

(ii) alternate formulation of II ;

(iii) structural isomers.

Both II and III are precipitated from boiling aqueous solution which appears to obviate the possibility of dimorphous forms. Alternate formulations of II are possible involving Pd–OH bonds and free carboxylic acid groups. Finally, since the compounds contain two asymmetrical sulphur atoms, they may be related as racemic and meso forms. On the limited amount of data obtained it is impossible to decide which formulation is correct.

The compound II was also prepared by the slow addition (one week) of a dilute aqueous solution of the sodium salt of o-methyl-mercaptobenzoic acid to a large excess of an ice cold solution of K_2PdCl_4. Thus the bridged compound was formed directly from the chelating acid without first precipitating out bis(o-methyl-mercaptobenzoato) palladium (II).

Although practically insoluble in water and organic solvents, the bridged compound II dissolved in sodium hydroxide solution, three equivalents being required per mole of bridged compound. Acidification of this solution with two equivalents of hydrochloric acid precipitated reddish brown crystals of a new compound, IV, which has been formulated as containing mixed bridging atoms.

A saturated aqueous solution of II which was only very sparingly soluble in water was found to have a pH of 4·5–4·8, indicating that considerable hydrolysis had taken place, possibly as given in Table 2. A suggested mechanism of the reaction of II with sodium hydroxide is given in Table 3. Compound II was found to be soluble in a concentrated solution of potassium chloride (cf. Chatt and Mann, 1939). However, no compound was isolated from the solution.

Heating of II with dilute hydrochloric acid yielded bis (o-methyl-mercapto-benzoic acid) palladium (II), V (Livingstone, Plowman and Sorenson, 1951). A 0·00025 M solution of V was found to have a pH of 3·6 ; this is the same pH value as hydrochloric acid of the same concentration. This confirms that the reaction, as given in Table 4, takes place in solution, since recrystallization of V from water yields VI (Livingstone, Plowman and Sorenson, 1951).

A bridged compound VII similar to III, but with bromine atoms in place of the chlorine, was prepared by a similar method to that used for III.

TABLE 1

Bis (o-methyl-mercaptobenzoate) palladium (II)

II Bis(o-methyl-mercaptobenzoate)-μ-dichloro-
    dipalladium (II), 2-hydrate
III Bis(o-methyl-mercaptobenzoate)-μ-dichloro-
    dipalladium (II)

Bis (o-methyl-mercaptobenzoate)-μ-monohydroxo-
monochloro-dipalladium (II)

Bis(o-methyl-mercaptobenzoate)-μ-dibromo-
dipalladium (II)

TABLE 2

TABLE 3

TABLE 4

Dichloro-bis (o-methyl-mercapto benzoic acid)-
palladium (II)

Monochloro-(o-methyl-mercaptobenzoate)
(o-methyl mercaptobenzoic acid)palladium (II)

On substituting trans-dichlorodiammine palladium (II), trans-diglycine palladium (II) (Pinkard, Sharratt, Wardlaw and Cox, 1934), bis (anthranilato) palladium (II) VIII, and bis(o-carboxy-phenyldimethylarsine) palladium (II) IX, in place of bis(o-methylmercapto-benzoato) palladium (II) I, no reaction with potassium chloropalladate (II) to form bridged compounds was observed. Mann and Purdie (1935) were able to prepare bridged palladium compounds with dichloro-bis(trialkyl-phosphine) palladium (II) and dichloro-bis (trialkyl-arsine) palladium (II) but not with the corresponding sulphur analogues. From these results it seems that the formation of μ-halogeno compounds of palladium is dependent on the nature of the attached ligand.

EXPERIMENTAL.

I. *Bis(o-methyl-mercaptobenzoato) palladium (II).*

Prepared by the reaction of potassium chloropalladate (II) on sodium o-methyl-mercapto-benzoate (Livingstone, Plowman and Sorenson, 1951). A $0·0025$ M solution of the compound was found to have a pH of $4·2$.

II. *Bis(o-methyl-mercaptobenzoato)-μ-dichloro-dipalladium (II) 2-hydrate.*

(*a*) To a solution of bis (o-methyl-mercaptobenzoato) palladium (II) (1 g.) in boiling water (180 ml.) was added, drop by drop over thirty minutes, an aqueous solution (40 ml.) of potassium chloropalladate (II) (0·97 g.). After twenty minutes at the boiling point crystals began to form. The deep orange tetragonal prisms were almost insoluble in hot water, only very slightly soluble in boiling alcohol, but insoluble in organic solvents. Yield $1·1$ g.; m.pt. $214°$ C.

When the compound, dried over P_2O_5, was heated in a closed tube, water was evolved at a temperature just below the melting point.

Found : Pd, $32·6\%$; Cl, $10·8\%$.

(*b*) An aqueous solution (90 ml.) of sodium o-methyl-mercaptobenzoate (2·3 g.) was added very slowly from a burette to an ice cold solution (270 ml.) of potassium chloropalladate (II) (15·6 g.). After six hours crystallization commenced; the total addition took six days. The product, washed with water and dried over P_2O_5, consisted of deep orange tetragonal prisms, m.pt. $214°$ C.; water evolved when heated to just below the melting point.

Found : Pd, $32·6\%$; Cl, $10·8\%$.

$[(C_8H_7O_2S)PdCl]_2.2H_2O$ requires : Pd, $32·60\%$; Cl, $10·83\%$.

III. *Bis(o-methyl-mercaptobenzoato)-μ-dichloro-dipalladium (II).*

To an aqueous solution (50 ml.) of potassium chloropalladate (II) (0·48 g.) was added slowly (20 min.) at the boiling point an aqueous solution (90 ml.) of bis(o-methyl-mercaptobenzoato) palladium (II) (0·5 g.). After ten minutes heating crystallization commenced. Yield $0·58$ g. The product, washed with water and dried over P_2O_5, consisted of pale yellowish brown prisms of m.pt. $224°$ C. No water was evolved on heating to decomposition.

Found : Pd, $34·2\%$; Cl, $10·9\%$.

$[(C_8H_7O_2S)PdCl]_2$ requires : Pd, $34·49\%$; Cl, $11·46\%$.

IV. *Bis(o-methyl-mercaptobenzoato)-μ-monohydroxo-monochloro-dipalladium (II).*

Bis(o-methyl-mercaptobenzoato)-μ-dichloro-dipalladium (II) 2-hydrate II (1·00 g.) was treated with $0·1$ N NaOH solution. It required $42·3$ ml. $0·1085$ N NaOH to dissolve completely (i.e., exactly three moles of NaOH to two moles of Pd). To this solution was added $28·0$ ml. $0·1089$ N HCl (i.e. two moles HCl to two moles of Pd). An amorphous brown precipitate formed, which, on standing overnight, crystallized into small reddish brown crystals which appeared to be cubic. Yield, $0·68$ g.

Found : Pd, $35·0\%$; Cl, $6·0\%$.

$(C_8H_7O_2S)_2Pd_2OHCl$ requires : Pd, $35·55\%$; Cl, $5·98\%$.

V. *Dichloro-bis(o-methyl-mercaptobenzoic acid) palladium (II).*

(a) A sodium hydroxide solution of bis (o-methyl-mercaptobenzoato)-μ-dichloro-dipalladium (II) 2-hydrate II (0·7 g.) was treated with excess hydrochloric acid (2 N) and reddish brown crystals were deposited, m.pt. 250° C.

Found :· Pd, 20·8% ; Cl, 13·7%.

Calculated for $(C_8H_8O_2S)_2PdCl_2$: Pd, 20·76% ; Cl, 13·80%.

The product could be recrystallized by digesting the mother liquor to yield reddish brown pyritohedra of m.pt. 250° C.

(b) On treating II with hydrochloric acid (2 N) and digesting for half an hour at the boiling point, reddish brown crystals were obtained, m.pt. 250° C.

Found : Pd, 21·0%.

A 0·00025 M solution was found to have a pH of 3·6.

VII. *Bis(o-methyl-mercaptobenzoato)-μ-dibromo-dipalladium (II).*

To a boiling aqueous solution (100 ml.) containing potassium bromopalladate (II) (1 g.) and potassium bromide (0·5 g.) was added a hot aqueous solution (200 ml.) of bis (o-methyl-mercaptobenzoato) palladium (II) (0·75 g.) over a period of 15 minutes. After 10 minutes crystals began to form ; after a further 15 minutes heating the red brown crystals were filtered hot, washed with hot alcohol, then acetone. Yield 0·85 g.

Found : Pd, 30·3% ; Br, 22·6%.

$[(C_8H_7O_2S)PdBr]_2$ requires : Pd, 30·16% ; Br, 22·59%.

VIII. *Bis(anthranilato) palladium (II).*

The reaction of anthranilic acid with Pd[II] has been investigated by Sheintsis (1939), who determined the sensitivity, but apparently did not characterize the compound.

Anthranilic acid (5·5 g.) was dissolved in aqueous sodium hydroxide solution (1·6 g. NaOH) and a solution of potassium chloropalladate (II) (6·5 g.) added in the cold. The yellow crystalline product was washed with water and acetone and dried, m.pt. 245° C.

Found : Pd, 27·8% ; N, 7·39%

$Pd(C_7H_6O_2N)_2$ requires : Pd, 28·16% ; N, 7·39%

IX. *Bis(o-carboxy-phenyl-dimethylarsine) palladium (II) 2-hydrate.*

o-Carboxy-phenyl-dimethylarsine (1·20 g.)—prepared by the method of Barclay and Nyholm (1947)—was dissolved in one equivalent of sodium hydroxide solution (30 ml.) and a solution (10 ml.) of potassium chloropalladate (II) (1·25 g.) added. The mixture was warmed for five minutes, then cooled. The yellow product was washed with water and recrystallized from water, m.pt. 178° C. When the compound, dried over P_2O_5, was heated, water was given off at a temperature just below decomposition.

Found : Pd, 18·15% ; C, 36·34% ; H, 3·94%.

$Pd(C_9H_{10}O_2As)_2.2H_2O$ requires : Pd, 18·00% ; C, 36·47% ; H, 4·08%.

SUMMARY.

Further investigations of the reactions of compounds of o-methyl-mercapto-benzoic acid with divalent palladium have shown that it is possible to prepare bridged halogeno compounds containing o-methyl-mercaptobenzoic acid as a chelating molecule. The μ-dichloro compound $[C_8H_7O_2SPdCl]_2$ was found to exist in two forms, with different colours and melting points, one anhydrous and the other hydrated. A corresponding dibromo analogue $[C_8H_2O_2SPdBr]_2$ was prepared in the anhydrous form. One of the chloro atoms in the μ-dichloro compound was replaceable by a hydroxo group to give a new complex $(C_8H_7O_2S)_2Pd_2OHCl$, containing mixed bridging groups. Various reactions of these compounds are discussed. Similar μ-halogeno compounds were not obtained with certain other ligands attached to the palladium.

REFERENCES.

Barclay, G. A., and Nyholm, R. S., 1947. THIS JOURNAL, **81**, 77.

Chatt, J., and Mann, F. G., 1939. *J.C.S.*, 1622.

Livingstone, S. E., Plowman, R. A., and Sorenson, J., 1951. THIS JOURNAL, **84**, 28.

Mann, F. G., and Purdie, D., 1935. *J. Soc. Chem. Ind.*, **54**, 814.

———————————————— 1936. *J.C.S.*, 873.

Mann, F. G., and Wells, A. F., 1938. *J.C.S.*, 702.

Pinkard, F. W., Sharratt, E., Wardlaw, W., and Cox, E. G., 1934. *J.C.S.*, 1012.

Sheintsis, O. G., 1938. *J. Gen. Chem. (U.S.S.R.)*, 8, 596.

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THE CHEMISTRY OF OSMIUM.

PART VIII. A NOTE ON THE PREPARATION OF AMMONIUM HEXACHLOROSMATE IV.

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and J. W. HOGARTH, A.S.T.C.

The alkali metal hexachlorosmates IV R_2OsCl_6 can be prepared by heating osmium tetroxide with hydrochloric acid. Chlorine is liberated slowly, some of the volatile tetroxide is lost and the acid H_2OsCl_6 results. A better method (Wintrebert, 1903) involves the formation of osmyl-oxy nitrite by reaction between the tetroxide and potassium nitrite. This substance, on addition to boiling hydrochloric acid, gives the potassium salt. Despite the claims of Wintrebert, the yield of potassium hexachlorosmate is never more than 40–50 per cent., reckoned on the weight of tetroxide used. The main source of the loss appears to be in the simultaneous formation of the very soluble potassium penta-nitro osmate III, with the osmyl-oxy nitrite.

Further, the decomposition of potassium osmyl-oxy nitrite is uncertain, the best results being obtained by the very slow addition of the substance to vigorously boiling acid.

Since the redox potential of the Os^{III}/Os^{IV} system in hydrochloric acid is 0·532 volt (Dwyer, Humpoletz and Nyholm, 1947), it can be concluded that ferrous salts should reduce osmium tetroxide in hydrochloric acid to the tetravalent stage and no further. When the reaction was carried out with ferrous chloride in concentrated hydrochloric acid, a deep orange solution of the acid H_2OsCl_6 resulted. Addition of ammonium chloride then gave an almost quantitative yield of analytically pure ammonium hexachlorosmate IV.

$$OsO_4 + 4FeCl_2 + 10HCl \rightarrow H_2OsCl_6 + 4FeCl_3 + 4H_2O$$

The alkali metal pentachlor-hydroxy osmates IV, $R_2[OsCl_5OH]$, were prepared by Krauss and Wilken (1924) from hydroxy-trichloro osmium IV. This series of complex salts can be obtained by reduction of osmium tetroxide with ferrous salts in controlled hydrogen and chloride ion concentrations. Although the reaction appeared to proceed quantitatively, the final yield was 30 per cent. of the theoretical, owing to the solubility of these complex salts, and the difficulty of removing ferrous and ferric salts. Only a trace of hexachlorosmate was formed. The pentachlor-hydroxy compounds are not intermediates in the formation of the hexachlorosmates. The ammonium salt $(NH_4)_2OsCl_5.OH$ could be boiled with concentrated hydrochloric acid in the presence of ammonium chloride without any ammonium hexachlorosmate resulting. This behaviour is similar to the ruthenium compounds $R_2[RuCl_5.OH]$, and confirms the observations of Mellor (1943) and Dwyer and Gibson (1950) on the hydrolysis of the hexachlorosmates.

$$OsO_4 + 4FeSO_4 + 2H_2SO_4 + 3HCl + 2NH_4Cl \rightarrow$$
$$(NH_4)_2OsCl_5OH + 2Fe_2(SO_4)_3 + 3H_2O.$$

EXPERIMENTAL.

Ammonium Hexachlorosmate IV.

Osmium tetroxide (1·0 g.) was heated with a mixture of ferrous chloride hexahydrate (10g.) and concentrated hydrochloric acid (30 ml.) in a stoppered flask on a water bath for 2 hours, with occasional shaking. The tetroxide rapidly dissolved and the deep greenish coloured solution became orange red. Ammonium chloride solution (20%—10 ml.) was added and the mixture cooled in ice. The deep red crystalline precipitate was filtered and washed with 80% alcohol and finally absolute alcohol. Yield : 1·6 g. ; 94%.

Found : Os 43·4%.

Calculated for $(NH_4)_2OsCl_6$: Os = 43·35%.

Ammonium Pentachlor-hydroxy Osmate IV.

A mixture of osmium tetroxide (1·0 g.), ferrous sulphate (5 g.), concentrated hydrochloric acid (3 ml.), sulphuric acid (10 N— 4 ml.), ammonium chloride (0·5 g.) and water (15 ml.) was heated on the water bath in a stoppered flask for two hours. After standing overnight, a very small quantity of red crystals of ammonium hexachlorosmate had been deposited. After filtration the deep greenish red solution was treated fractionally with 20% ammonium chloride solution to give a greenish brown precipitate of the pentachlor-hydroxy salt. Finally the solution was treated with 2 g. of solid ammonium chloride and 10 ml. of concentrated hydrochloric acid and evaporated nearly to dryness. Sufficient water was added to dissolve the ferric salts and the mixture filtered to give a further crop of the substance. This was finally dissolved in the minimum volume of warm water and precipitated by the addition of ammonium chloride. The dark greenish brown crystals were washed with 90% alcohol. Yield : 0·5 g. ; 30%.

Found : Os — 45·4% ; Cl = 42·19%.

Calculated for $(NH_4)_2[OsCl_5.OH]$: Os = 45·21% ; Cl — 42·19%.

SUMMARY.

Ammonium hexachlorosmate was obtained in almost quantitative yield from osmium tetroxide by reduction with ferrous chloride and hydrochloric acid, followed by addition of ammonium chloride. Ammonium pentachlorhydroxy osmate was obtained in a similar manner by using ferrous sulphate as the reducing agent.

REFERENCES.

Dwyer, F. P., Humpoletz, J. A., and Nyholm, R. S., 1947. THIS JOURNAL, **80**, 242.
Dwyer, F. P., and Gibson, N. A., 1950. *Nature*, **165**, 1012.
Krauss, F., and Wilken, D., 1924. *Z. anorg. Chem.* **137**, 360.
Mellor, D. P., 1943. THIS JOURNAL, **77**, 145.
Wintrebert, 1903. *Ann. de Chim. de Phys.*, **28**, 121.

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THE ESSENTIAL OILS OF *ZIERIA SMITHII* (ANDREWS) AND ITS VARIOUS FORMS.

PART II.

By F. R. Morrison,
A. R. Penfold
and Sir John Simonsen.

The results of examination of the essential oils of this small Rutaceous shrub, which occurs in moist situations throughout New South Wales, Victoria and Queensland, were first published in 1930 (Penfold, 1925). The oils proved to be a very remarkable series, rich in the phenol ethers, safrole, methyl eugenol and elemicin.

The variation in chemical composition, and the probable occurrence of physiological forms, made it desirable for publication at that date to be restricted to the results obtained with material growing in Queensland. These oils consisted mainly of safrole with some methyl eugenol. The investigation has been continued for over twenty-five years, but has only recently been completed.

One constituent of unusual interest was isolated from the essential oil obtained from plants collected in New South Wales. This substance, l-$\triangle^3$-carene-5 : 6-epoxide (I) was investigated by Penfold, Ramage and Simonsen (1939) and is closely related to l-$\triangle^3$-carene (II). It is thus the third substance containing the carane ring to be found in nature.

I   II

Carene-epoxide appears to be present in greatest amount in the plants collected from the Bellinger River district of New South Wales. This is evident from the lævo-rotation of the crude oils distilled from that material.

Our botanical material was carefully examined by Mr. E. Cheel when Curator of the National Herbarium, Botanic Gardens, Sydney, in 1927. Although identified as *Zieria smithii*, Mr. Cheel expressed the opinion that the Bellinger River material differed sufficiently in morphological characters from the type to be considered a definite form. Pending agreement by botanists, we propose distinguishing the Bellinger River plant by naming it *Zieria smithii* variety " *A* ". The present paper deals with the chemistry of the essential oils obtained from material collected in various parts of New South Wales.

The principal constituents so far identified are as follows, viz. :

Safrole, methyl eugenol, elemicin, d-α-pinene, l-△^{3}-carene-5 : 6-epoxide, linalool and eugenol. An unidentified alcohol, $C_{10}H_{14}O$, and nopinone (?) are also present.

The phenol ethers occur singly or in admixture ; in some instances all three occur together as observed with the oils obtained from the Bellinger River and Lilyvale. The occurrence of the three phenol ethers, mentioned in varying proportions in the foliage from different localities, is of unusual interest. Although in some instances one particular phenol ether may predominate, namely safrole, methyl eugenol or elemicin, to the extent of 80%–90%, it is usually accompanied by a small quantity of one of its associates.

The yields of oil varied from 0·5% to 1·2%, calculated on the freshly cut leaves and terminal branchlets.

EXPERIMENTAL.

Three thousand five hundred and forty-eight pounds weight of leaves and terminal branchlets, collected in various parts of New South Wales, were subjected to steam distillation. The distillates were usually pale yellow oils, heavier than water, highly refractive, and they possessed the characteristic odour of the phenol ethers, modified by that of carene-epoxide.

It was practicable, in the course of distillation of the leaves, to separate the portion of oil lighter than water from the heavier-than-water fraction. This separation proved useful in isolating and identifying the lower boiling constituents. A typical example is given under the heading of l-△^{3}-carene-5 : 6-epoxide in the appended table. Unless otherwise stated, the chemical and physical constants were taken on the mixed distillates.

It would be impracticable to record the results of examination of the oils from each consignment. For the purpose of this paper one or two are selected as typical examples.

The oil from a consignment of leaves collected at Toronto, New South Wales, on 27th January, 1925, was subjected to fractional distillation under reduced pressure, with the following results, viz. :

100 ml. crude oil taken.

B.P./10 mm.	Volume. (Ml.)	$d\frac{15°}{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$
50– 90°	20	0·8677	1·4662	+37·2°
90–126°	20	1·0027	1·5092	—1°
126–150°	50	1·0652	1·5285	—0·55°
Residue	6			

On redistillation, the following fractions were finally obtained :

B.P.	Volume. (Ml.)	$d\frac{15°}{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$
153–158°/766 mm. ..	10	0·8596	1·4653	+43·6°
50–100°/ 10 mm.	4	0·8829	1·4703	+23·4°
100–110°/ 10 mm.	6	0·9640	1·4938	—3·4°
110–140°/ 10 mm.	14	1·0479	1·5253	—1·5°
140–150°/ 10 mm.	30	1·0650	1·5294	±0°

TABLE 1.

Zieria smithii (Andrews) from New South Wales.

Date.	Locality in New South Wales.	Weight of Leaves.	Yield of Oil.	$d_{15°}^{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$	Solubility in 70% Alcohol. (W./W.)	Ester No. 1¼ Hours Hot Sap.	Ester No. after Acetylation.	Principal Constituents.	Remarks.
		Lb.	%								
27/ 9/1923	Terrigal (Official Collector).	32¾	1·1	1·0382	1·5136	+9·2°	Vol. 8·5	58·0	128·6	Safrole.	
14/ 2/1924	Narrabeen.	4	1·2	1·0321	1·5273	+0·85°	1·0	—	—	Methyl eugenol.	
15/ 2/1924	Terrigal.	89	0·71	1·0407	1·5145	+4·0°	7·5	—	—	Safrole.	
27/ 1/1925	Toronto.	135	0·67	1·0064	1·5102	+6·0°	1·0	5·5	36·43	Elemicin and safrole.	
9/ 9/1925	Condong (H. Johnson).	76	0·45	1·022	1·5111	+9·4°	0·9	36·5	89·00	Safrole and methyl eugenol.	
12/ 7/1926	Bellinger River (A. J. Washington).	39	1·57	1·0085	1·5084	-18·1°	0·9	81·5	106·00	Methyl eugenol and elemicin.	Variety "A".
7/ 3/1927	Bellinger River (A. J. Washington).	77	1·06	1·011	1·5084	-11°	1·0	78·2	107·2		Variety "A".
12/ 8/1927	Bellinger River (A. J. Washington).	53	1·6	1·0122	1·5093	-8·4°	1·0	77·2	105·00	Methyl eugenol and elemicin.	Variety "A" in full flower.
16/ 7/1930	Bellinger River (W. P. Tyson).	130	0·80	1·0136	1·5100	-4·25°	0·8	—	104·4		Identified by E. Cheel as a form of the type (var. "A"). Portion lighter than water.
18/ 8/1930	Bellinger River (F. Gale).	160	0·38 / 0·63	0·9863 / 1·0187	1·4950 / 1·5135	-29·8° / -3·8°	0·9 / 0·9	158·3 / 53·1	172·0 / 71·6		Portion heavier than water (var. "A"). Variety "A".
29/10/1934	Bellinger River (W. P. Tyson).	215	1·29	0·9978	1·5022	-3·2°	0·9	100·0	115·8	Safrole, methyl eugenol and elemicin.	
16/ 6/1936	Bellinger River (W. P. Tyson).	1438¾	1·4	0·9896	1·4996	-5·0°	0·9	97·4	150·2		
31/ 8/1936	Bellinger River (W. P. Tyson).	1010	1·18	0·9857	1·4981	+0·6°	1·0	105·2	149·1	Safrole, methyl eugenol and elemicin.	
19/ 8/1947	Condong (Colonial Sugar Refining Co.).	80	0·47	1·012	1·5120	-0·92°	10·0	41·4	61·6	Safrole and methyl eugenol.	
8/ 9/1947	Newport, near Sydney.	27	0·9	1·005	1·5076	+7·25°	1·5	36·0	69·0	Safrole, methyl eugenol and elemicin.	
14/ 7/1949	Newport, near Sydney.	69¾	0·13	1·017	1·5102	+5·00°	3·0	—	—	Safrole, methyl eugenol and elemicin.	
21/ 7/1949	Narrabeen, near Sydney	6¾	0·73	1·025	1·5220	+2·75°	0·7	—	—	Methyl eugenol.	
21/ 7/1949	Palm Beach.	27	0·59	1·007	1·5198	-1·90°	1·0	—	—		
18/ 8/1949	Lilyvale.	81	0·21	1·017	1·5221	-0·65°	1·0	22·3	36·1	Methyl eugenol (80%), safrole (under 10%).	

Determination of d-α-pinene.

2 Ml. of the fraction distilling at 153–158°/766 mm. on mixing with an equal volume of *l*-α-pinene gave an excellent yield of pinene nitrosochloride, m.p. 109°, raised by recrystallization to 115°. 8 ml. on oxidation with potassium permanganate (Penfold, 1922*a*), yielded pinonic acid m.p. 69–70° $[\alpha]_D^{20°} = +90\cdot1°$ (in $CHCl_3$, $C = 3.3$) The semicarbazone of the acid had m.p. 208°.

Determination of Safrole.

The fractions distilling at 100–110° and 110–140°/10 mm. were mixed together and placed in a bath of solid carbon dioxide ; the frozen mass was transferred to a Buchner filter funnel surrounded by a mixture of ice and salt. By continued repetition of this process the principal constituent, safrole, was separated, and purified by fractional distillation. It possessed the following physical and chemical characters : b.p. 230–233°/762 mm., m.p. 11°, $d_{15°}^{15°}$ $1\cdot1046$, $n_D^{20°}$ $1\cdot5375$, $\alpha_D^{20°}$ $-0\cdot2°$.

10 g. of the safrole were oxidized with potassium permanganate in accordance with the method described (Penfold, 1925, p. 87) and gave a good yield of piperonylic acid m.p. 228°, both alone and in admixture with an authentic specimen.

Determination of Elemicin.

The fraction distilling between 140° and 150°/10 mm. was oxidized with potassium permanganate in alkaline solution in accordance with the procedure described by Penfold (1922*b*). Two acids were obtained, trimethyl gallic, m.p. 169–170°, and trimethyl-homogallic, m.p. 119–120°, which placed the identity of the phenol ether as elemicin beyond doubt. Mixed melting points showed no depression.

Leaves Collected at Terrigal, New South Wales.

Oil from a consignment of leaves collected at Terrigal on 15th February, 1924, was subjected to fractional distillation under reduced pressure, with the following results, viz. :

100 ml. of crude oil, after removal of all alkali-soluble substances with 8% sodium hydroxide solution, gave the following results on distillation :

B.P.	Volume. (Ml.)	$d_{15°}^{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$
50– 60°/10 mm.	7	0·8635	1·4664	+39·45°
60–105°/10 mm.	8	0·9488	1·4865	+21·5°
105·5–109°/10 mm.	26	1·0495	1·5140	+7·5°
109·5–112°/4–5 mm.	45	1·0815	1·5261	+3·7°
Residue	14	—	—	—

Determination of d-α-pinene.

Similar results were obtained with the first fraction as in the examination of the oil from Toronto, 27th January, 1925.

Determination of Safrole.

Safrole was separated from the second and third fractions by the method described above, and had m.p. 11°, $d_{15°}^{15°}$ $1\cdot1031$, $n_D^{25°}$ $1\cdot5339$, α_D $+0\cdot85°$. It was converted to isosafrole by treatment with sodium ethoxide in ethyl alcohol. The isosafrole subsequently isolated possessed the following constants : b.p. 120·5–122°/10 mm., $d_{15°}^{15°}$ $1\cdot123$, $n_D^{20°}$ $1\cdot5740$. It was oxidized with chromic acid in glacial acetic acid solution to piperonal. The crude aldehyde was purified through the bisulphite compound, and, on recrystallization from ethyl alcohol, had m.p. 37°, both alone and in admixture with an authentic sample.

Determination of Nopinone (?).

The first fraction, after washing with 50% resorcin solution, yielded 1 ml. of oil having $n_D^{14 \cdot 5°}$ 1·4760. It was converted to the semicarbazone, which, after recrystallization from ethyl alcohol, had m.p. 189–190°, both alone and in admixture with an authentic sample.

Found : C, 61·46 ; H, 9·07. $C_{10}H_{17}ON_3$ requires : C, 61·53 ; H, 8·7.

The identity of this ketone requires confirmation, since it has not previously been found to occur in nature. The rapid extermination of this plant in settled areas makes further collection difficult.

Determination of Linalool and Unidentified Alcohol, $C_{10}H_{14}O$.

The presence of a small percentage of linalool in this oil was established by the preparation of the xenyl urethane m.p. 83–85°, both alone and in admixture with an authentic example (Penfold, Ramage and Simonsen, 1939).

An unidentified alcohol was characterized by the preparation of its 3 : 5-dinitrobenzoate, m.p. 119° (Penfold, Ramage and Simonsen, 1939).

Minor Constituents.

Eugenol, to the extent of 2% of the crude oil, was isolated from the alkali-soluble substances in the usual way, and the benzoate prepared. It had m.p. 69–70°, both alone and in admixture with an authentic sample.

Volatile Acids—Acetic and Citronellic (?).

Small amounts of volatile acids, both free and combined, were isolated after saponification of the oil. Silver salt of water-soluble acid gave 63·8% Ag. $C_2H_3O_2Ag$ requires 64·67% Ag. A volatile oily acid was obtained, the silver salt of which gave 38·52% Ag. $C_{10}H_{15}O_2Ag$ requires 38·99% Ag.

Determination of l-$\triangle^3$-carene-5 : 6-epoxide.

This substance was found to occur in the oils obtained from the leaves and terminal branchlets collected from the Bellinger River district of New South Wales ; it is the principal constituent of the fraction boiling below 100°/10 mm.

The fraction of boiling point 88–90°/17 mm., on digestion with alkali, or if heated with water at 150°, gave geranic acid practically in quantitative yield. After removal of impurities such as linalool and the unidentified alcohol $C_{10}H_{14}O$, referred to above, the oil gave figures on analysis in close agreement with those required for $C_{10}H_{14}O$. This substance was l-$\triangle^3$-carene-5 : 6-epoxide, a colourless sweet smelling oil having the constants, b.p. 83–85°/14 mm., $d_{25°}^{25°}$ 0·9454, $n_D^{25°}$ 1·4729, $[\alpha]_{5461}$ −88°. Its structure and properties have been discussed elsewhere (Penfold, Ramage and Simonsen (1939) ; Penfold and Simonsen (1942)).

Leaves Collected at Fernmount, Bellinger River, 12th July, 1926. Determination of Methyl Eugenol.

The crude oil, on distillation, yielded a fraction possessing the following constants :

B.p. 130–135°/10 mm., $d_{15°}^{15°}$ 1·0435, $n_D^{20°}$ 1·5274, $\alpha_D^{20°}$ 1·5°.

6 Ml. on oxidation with potassium permanganate (Penfold, 1925) gave an excellent yield of veratric acid m.p. 179–180°, unaltered in admixture with an authentic specimen.

Fractions boiling from 135–147°/10 mm. were found to consist principally of elemicin. Oxidation with potassium permanganate in alkaline solution gave trimethyl gallic acid, m.p. 169–170°, and trimethyl-homogallic acid, m.p. 119 to 120°. Mixed melting points showed no depression.

The presence of safrole was not detected in this sample of oil.

SUMMARY.

The essential oils of *Zieria smithii*, a Rutaceous shrub found growing in moist situations throughout Queensland, New South Wales and Victoria, consist principally of one or more of the phenol ethers, safrole, methyl eugenol and elemicin. The oils obtained from plants growing in New South Wales contain also d-α-pinene, l-$\triangle^3$-carene-5 : 6-epoxide, linalool, an unidentified alcohol $C_{10}H_{14}O$, and nopinone (?). The chemistry of the latter oils is described in this paper.

REFERENCES.

Penfold, A. R., 1925. THIS JOURNAL, **64**, 83.
——————— 1922a. *Ibid.*, **56**, 195.
——————— 1922b. *Ibid.*, **56**, 128.
Penfold and Simonsen, 1942. *J.C.S.*, 206.
Penfold, Ramage and Simonsen, 1939. *J.C.S.*, 1496.

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  London.

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